

Laser Assisted Plasma Spectrochemistry

Laser Ablation

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2004 Winter Plasma Conference on
Plasma Spectrochemistry

Fort Lauderdale, Florida
January 7, 2004

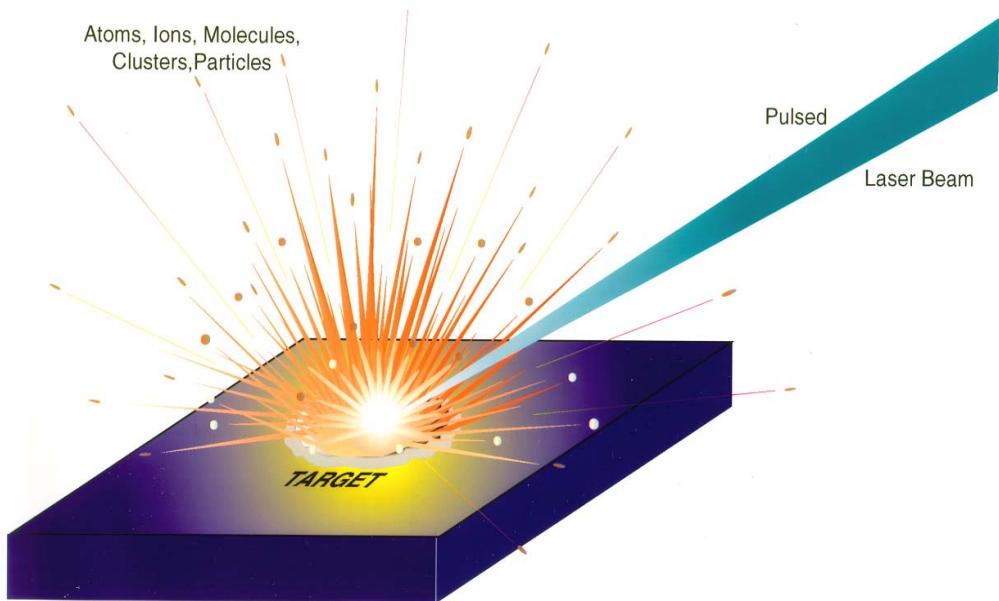
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Outline



- * **Introduction – applications**
- * **Analytical Issues**
- * **Some fundamentals**
- * **Shadowgraph imaging**
- * **Spectroscopic imaging**
- * **Femtosecond ablation**
- * **New Direction**
- * **Conclusion**

Laser Ablation



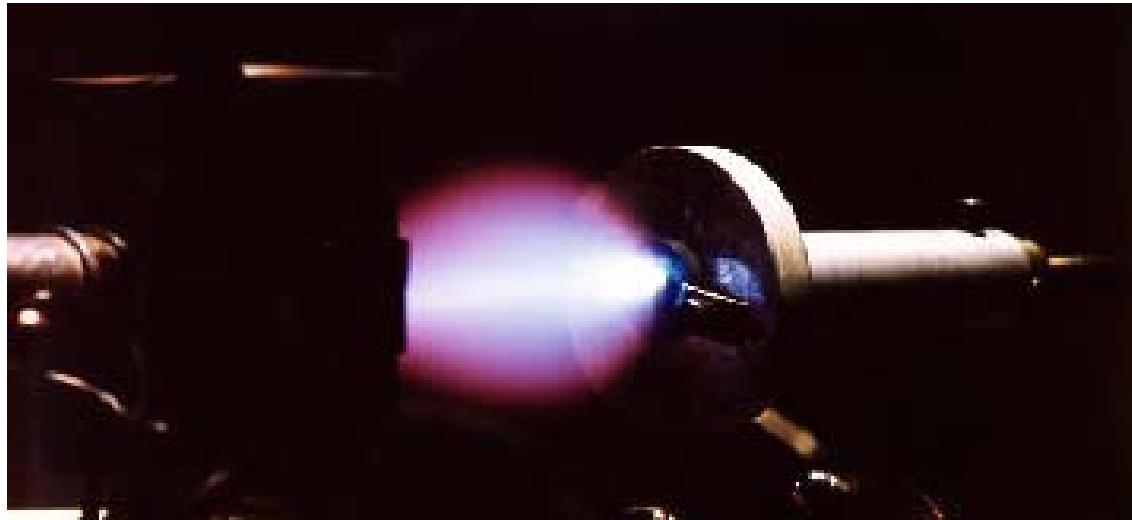
Approx 1,000 papers/year last 10 years

Applications

- Pulsed Laser Deposition
- Nanotechnology
- Medical
- Micromachining
- X-ray lasers
- Electron accelerators
- Chemical Analysis

Applications based on empirical basis!

Pulsed Laser Deposition



Fabrication of thin films from ‘any’ material; unique material structures

Applications: superconductivity, photovoltaic, electrodes, catalysts,

“Laser ablation is stoichiometric” – Materials Science community

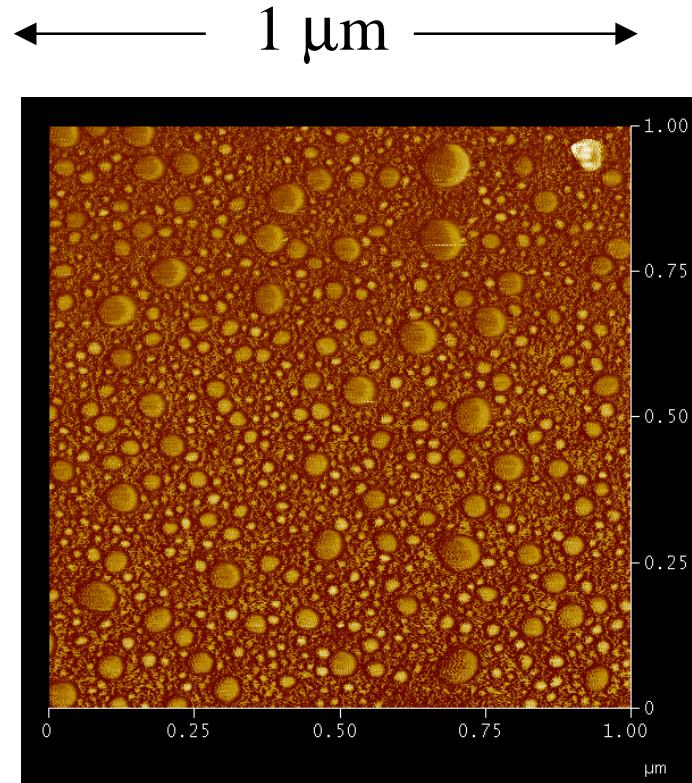
PLD not at atmospheric pressure!

Nanomaterials



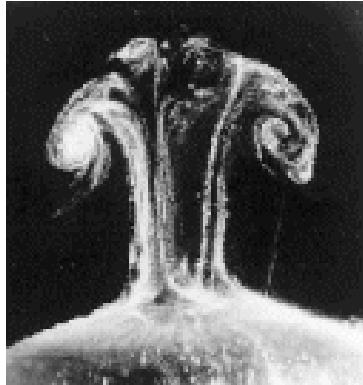
- Laser ablation used to form nanoparticles!
 - spheres, tubes, wires

Chemistry and size of particles determined by laser, sample, and environment properties!

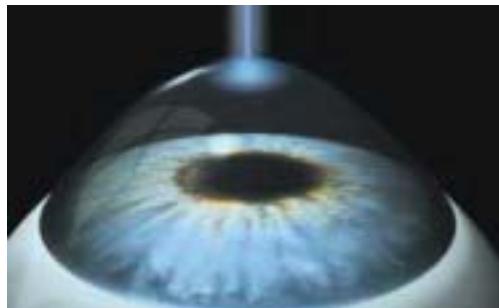


Atomic Force Microscope (AFM) image of brass nanoparticles on silicon substrate.

Medical



Tiny particles of the cornea evaporate,
allowing a contact-free ablation.



LASIK



Tatoo removal

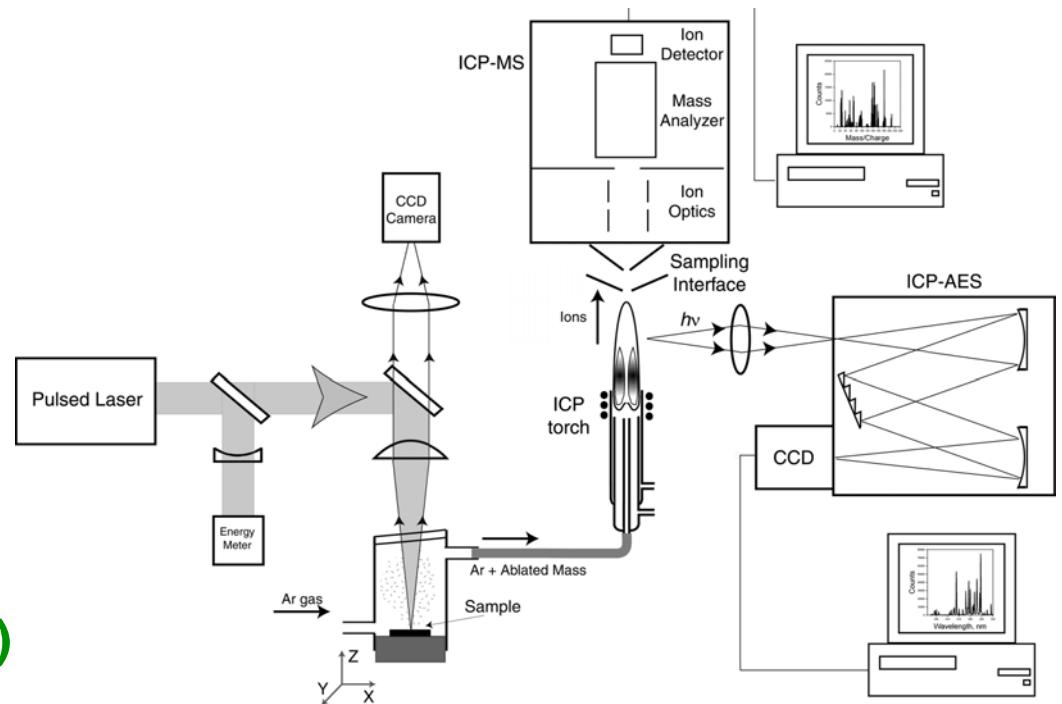
**Angioplasty, Surgery, Podiatry, Prostate,
ENT, Dentistry.....**

Laser Ablation for Chemical Analysis



Ablate unknown sample – analyze vapor

- Direct solid analysis
- Any solid sample
- No sample preparation
- Small sample quantity
- No solvents
- Spatial (micro) analysis
- Rapid, real-time analysis
- Laboratory analysis (ICP-MS)
- Field analysis (LIBS)

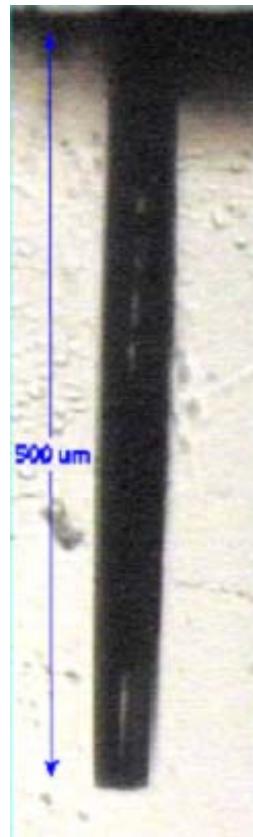


Laser ablation is faster, less expensive, easier, and safer than classical liquid dissolution!!!!

Laser Ablation Sampling



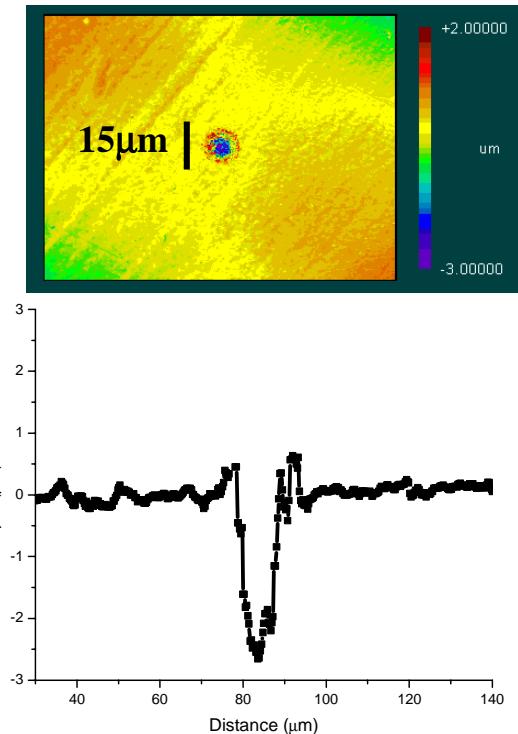
Micro channel
in glass



Spatial hair
analysis



Thin film depth
profiling



Issues



Accuracy: fractionation - absolute (single pulse) and crater related

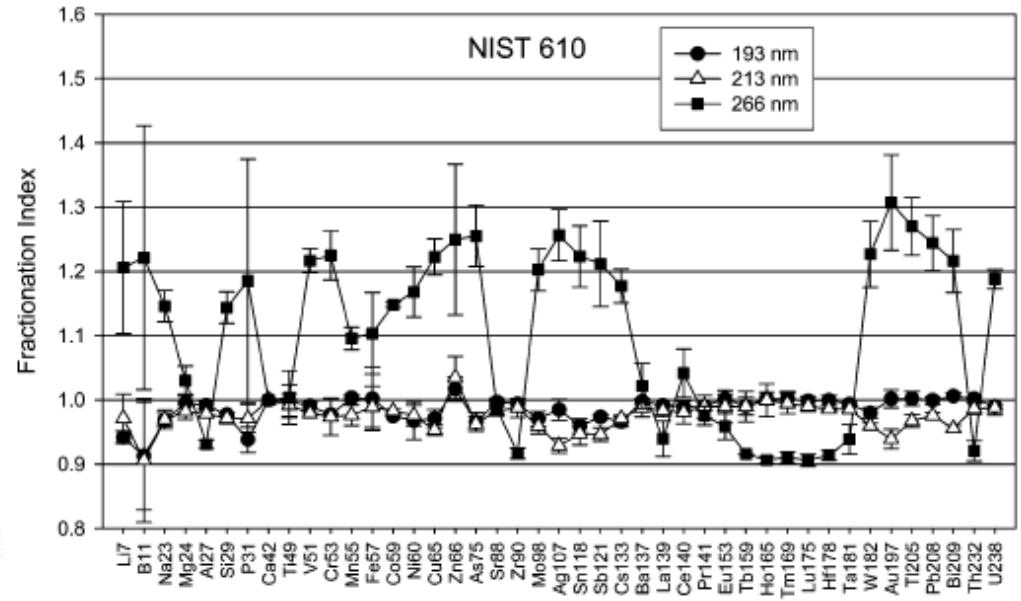
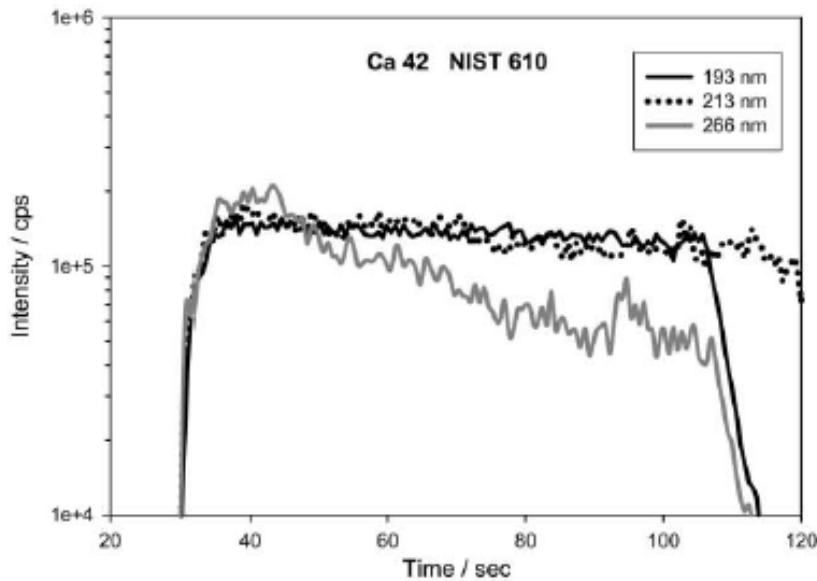
Precision: ablation-rate repeatability

Matrix dependence: ablated quantity related to material properties

- Laser (**type, wavelength, pulse duration, energy, intensity**)
- Environment (**gas, pressure**)
- Particles (**size, chemistry, size distribution, transport**)
- ICP and MS
- ???

Purchased an ICPMS as an expensive detector to study LA at atmospheric pressure- told that it was ‘a good source to digest all mass!’

Wavelength



Guillong M. Horn I. Gunther D. A comparison of 266 nm, 213 nm and 193 nm produced from a single solid state Nd : YAG laser for laser ablation ICP-MS. Journal of Analytical Atomic Spectrometry. 18(10):1224-1230, 2003.

Particles

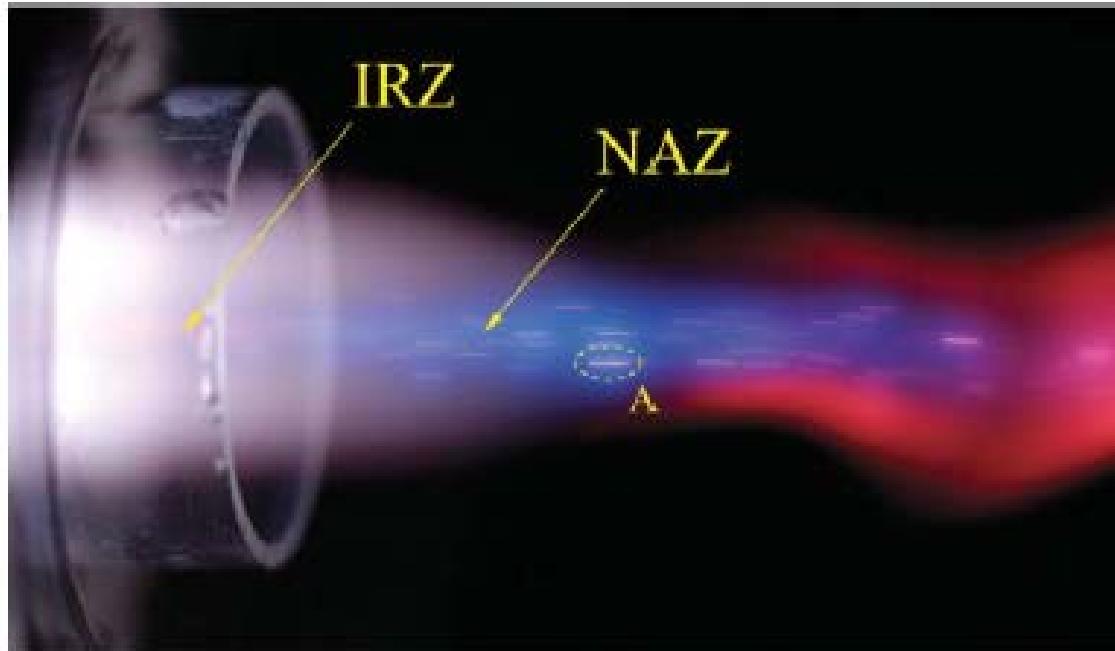


Fig. 2 A high-speed image of the ICP during 266 nm laser ablation of a Y₂O₃ pellet using argon as the sample-transport gas. Note red initial radiation zone (IRZ), blue normal analytical zone (NAZ), and large particle track (encircled, labeled A).

Aeschliman DB, Bajic SJ, Baldwin DP, Houk RS. High-speed digital photographic study of an inductively coupled plasma during laser ablation: comparison of dried solution aerosols from a microconcentric nebulizer and solid particles from laser ablation. [Article] Journal of Analytical Atomic Spectrometry. 18(9):1008-1014, 2003.

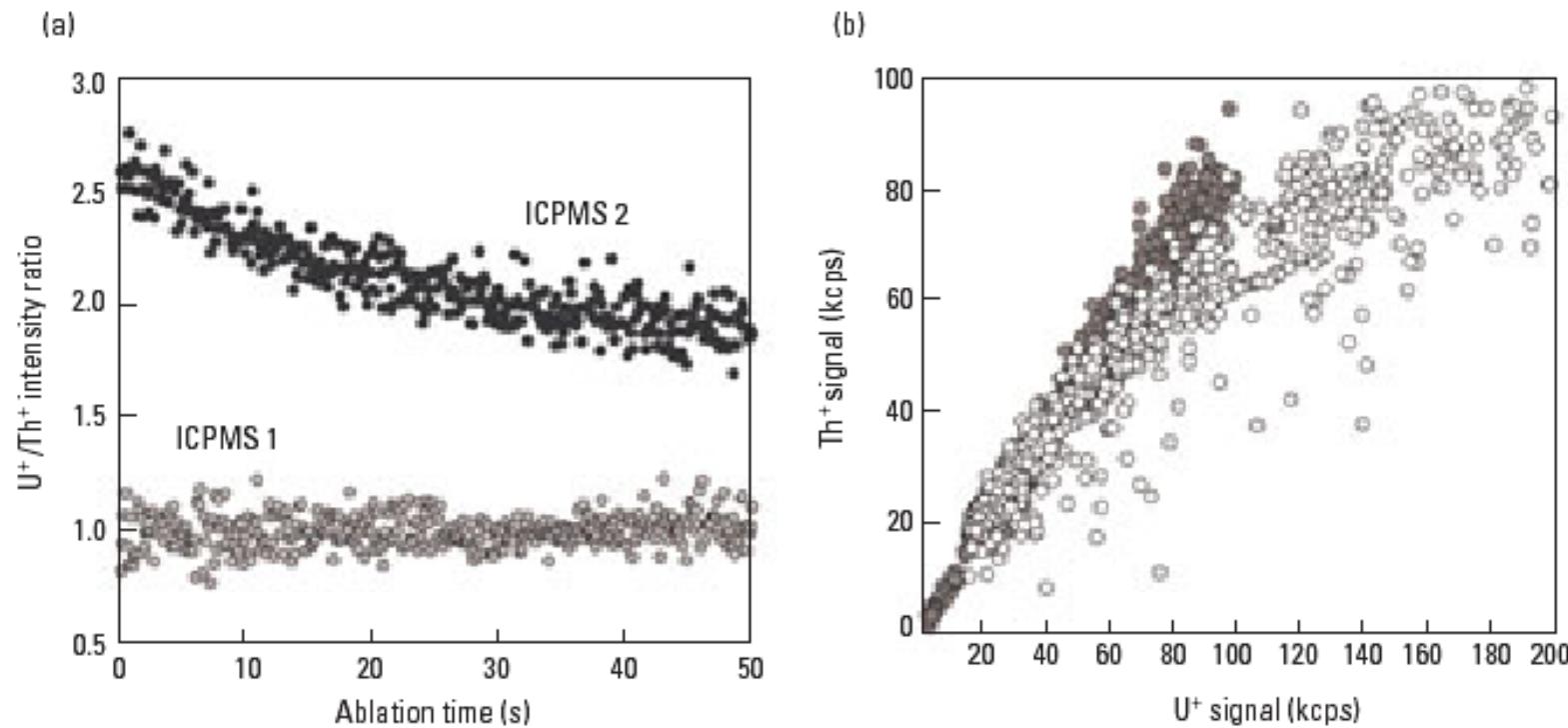


FIGURE 3. Thorium and uranium.

(a) Transient signal ratios for Th^+ and U^+ measured on two different instruments using identical ablation conditions. The significant offset and variation of this ratio for ICPMS 2 is an indication of incomplete atomization and ionization of Th^+ . (b) Correlation of thorium and uranium signal intensities during single-spot ablation at 266 nm. Open circles represent the intensities for a nonfiltered aerosol, where a significant deviation occurs. The filled circles indicate the higher correlation obtained after filtering the aerosol.

Hattendorf B. Latkoczy C. Gunther D. Laser ablation-ICPMS. Analytical Chemistry. 75(15):341A-347A, 2003.

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Fractionation

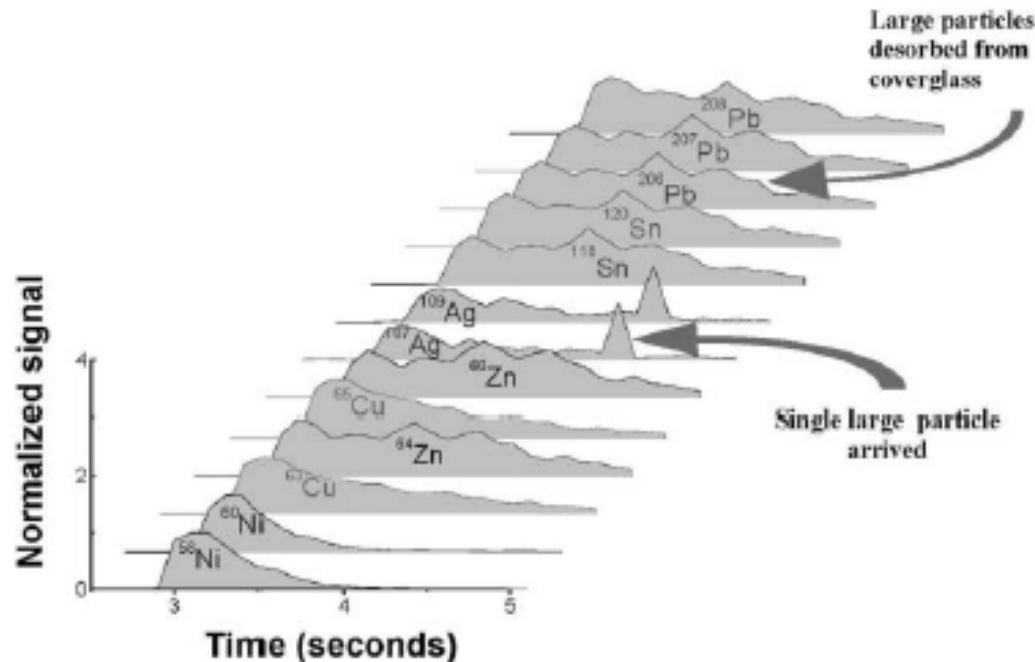


Fig. 2 Single laser shot fractionation effects. Normalized time scans of isotopes at 0.1 s intervals, resulting from a second laser shot on a sample coin (main elements are Cu, Ni, and Zn) are shown.

Kozlov B. Saint A. Skroce A. Elemental fractionation in the formation of particulates, as observed by simultaneous isotopes measurement using laser ablation ICP-oa-TOFMS. *Journal of Analytical Atomic Spectrometry*. 18(9):1069-1075, 2003.

Transport

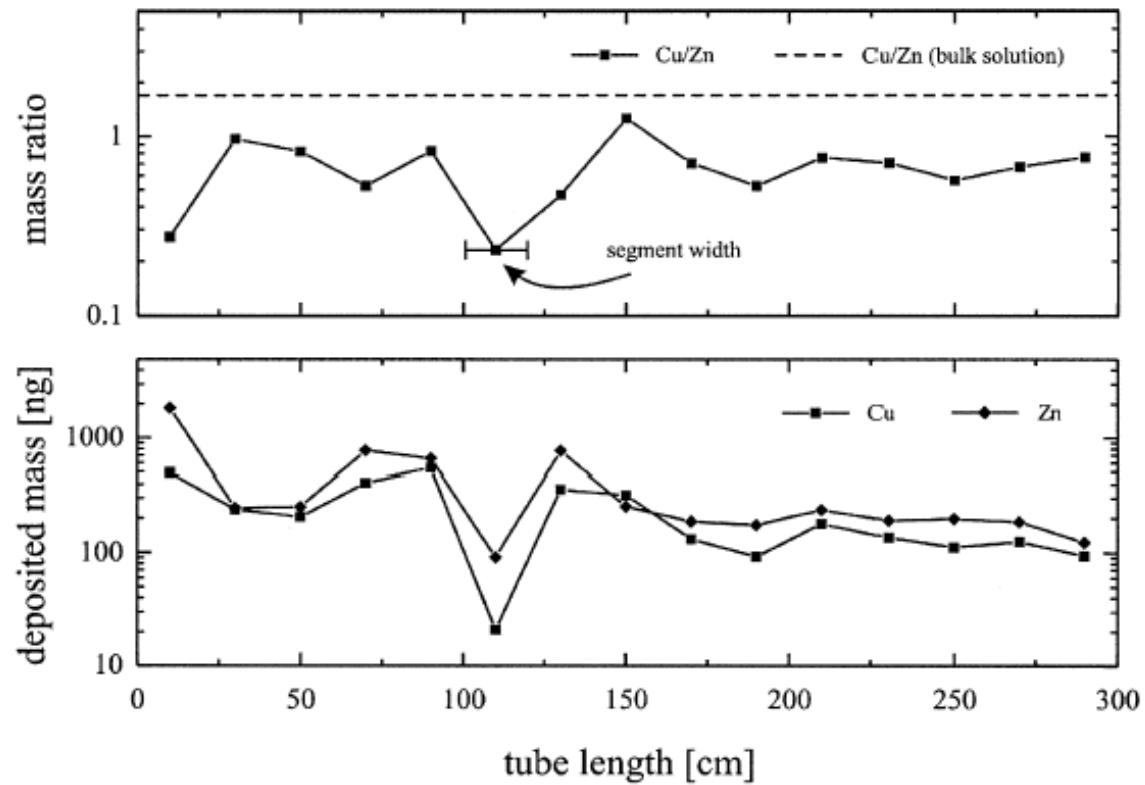


Fig. 5. Deposited Cu- and Zn-specific mass and the corresponding Cu/Zn element ratio in dependence on the tube length (Ar).

J.Koch, I.Feldmann, N.Jakubowski, K.Niemax, Elemental composition of laser ablation aerosol particles deposited in the transport tube to an ICP. Spectrochimica Acta Part B 57 (2002) 975–985

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???

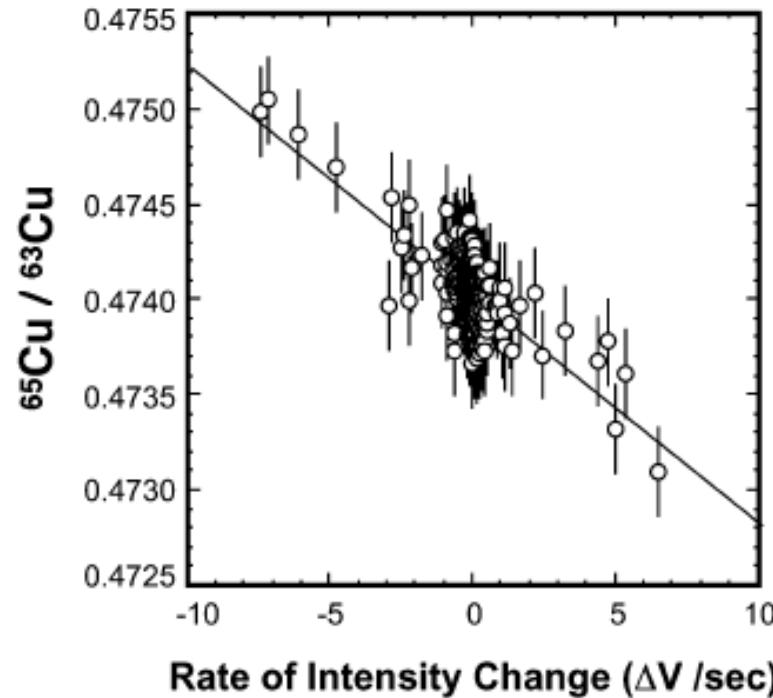


Fig. 2 Correlation between measured $^{65}\text{Cu}/^{63}\text{Cu}$ ratio and rate of intensity change (V s^{-1}). The data points shown here were obtained by solution analysis (Fig. 1). Simple linear correlation can be seen between the measured $^{65}\text{Cu}/^{63}\text{Cu}$ ratio and rate of intensity change.

Hirata T. Hayano Y. Ohno T. Improvements in precision of isotopic ratio measurements using laser ablation-multiple collector-ICP-mass spectrometry: reduction of changes in measured isotopic ratios. *Journal of Analytical Atomic Spectrometry*. 18(10):1283-1288, 2003.

Sample 2003 Publications



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- Erel E. Aubriet F. Finqueneisel G. Muller JF. Capabilities of laser ablation mass spectrometry in the differentiation of natural and artificial opal gemstones. *Analytical Chemistry*. 75(23):6422-6429, 2003.
- Dimov SS. Chrysoulis SL. Lipson RH. Quantitative elemental analysis for rhodium and palladium in minerals by time-of-flight resonance ionization mass spectrometry. *Analytical Chemistry*. 75(23):6723-6727, 2003.
- Hola M. Kanicky V. Mermet JM. Otruba V. Direct solid analysis of powdered tungsten carbide hardmetal precursors by laser-induced argon spark ablation with inductively coupled plasma atomic emission spectrometry. *Analytical & Bioanalytical Chemistry*. 377(7-8):1165-1174, 2003.
- Eggins SM. Laser ablation ICP-MS analysis of geological materials prepared as lithium borate glasses. *Geostandards Newsletter*. 27(2):147-162, 2003.
- Uryu T. Yoshinaga J. Yanagisawa Y. Endo M. Takahashi J. Analysis of lead in tooth enamel by laser ablation-inductively coupled plasma-mass spectrometry. *Analytical Sciences*. 19(10):1413-1416, 2003.
- Mateo MP. Cabalin LM. Laserna J. Line-focused laser ablation for depth-profiling analysis of coated and layered materials. *Applied Optics*. 42(30):6057-6062, 2003.
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- Gillanders BM. Kingsford MJ. Spatial variation in elemental composition of otoliths of three species of fish (family Sparidae). *Estuarine Coastal & Shelf Science*. 57(5-6):1049-1064, 2003.
- Tibi M. Heumann KG. Multi-element trace determinations in pure alkaline earth fluoride powders by high-resolution ICP-MS using wet-chemical sample preparation and laser ablation. *Analytical & Bioanalytical Chemistry*. 377(1):126-131, 2003.
- Seltzer MD. Laser ablation inductively coupled plasma mass spectrometry measurement of isotope ratios in depleted uranium contaminated soils. *Applied Spectroscopy*. 57(9):1173-1177, 2003.
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- Chan GCY. Chan WT. Plasma-related matrix effects in inductively coupled plasma - atomic emission spectrometry by group I and group II matrix-elements. *Spectrochimica Acta Part B-Atomic Spectroscopy*. 58(7):1301-1317, 2003.

Sample 2003 Publications



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- Hobbs AL. Almirall JR. Trace elemental analysis of automotive paints by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). *Analytical & Bioanalytical Chemistry*. 376(8):1265-1271, 2003.
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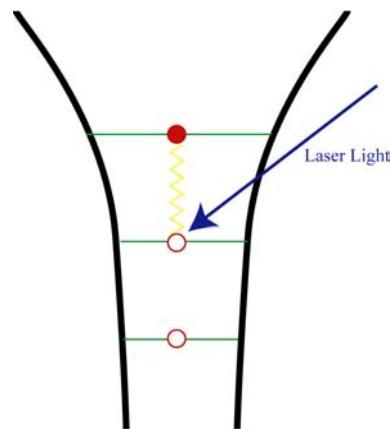


Laser Ablation?

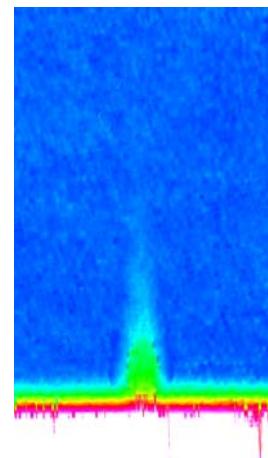
Laser Ablation Time Scale



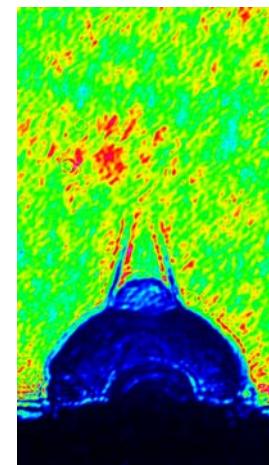
Electrons absorb
photons -
femtoseconds



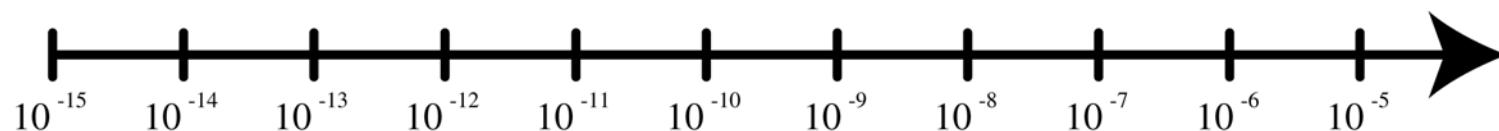
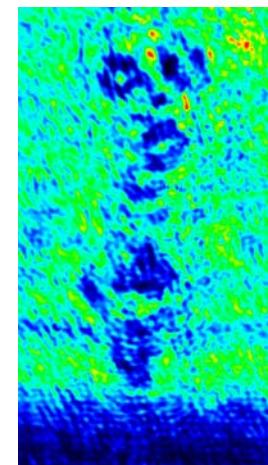
Electron emission
from surface -
picoseconds



Plasma formation
- nanoseconds



Particle ejection
- microseconds

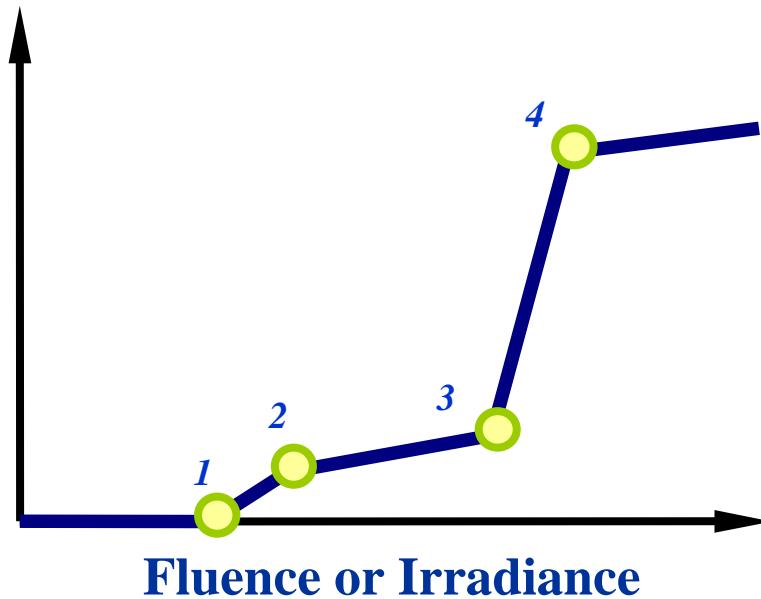


Time (seconds)

Laser Ablation



ICP Intensity
LIBS Intensity
Plasma Properties
Crater Properties
Plume Image



Complexity:

LMI = non-linear processes

Laser-plasma interaction

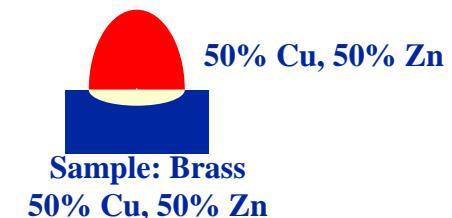
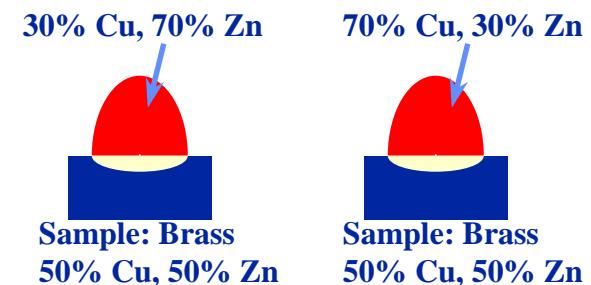
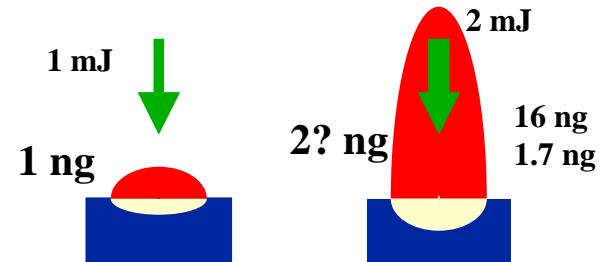
Plasma-sample interaction

Particles (size, size distribution, chemistry)

Ablated Mass



- **Quantity of ablated mass**
 - Amount of ablated mass depends non-linearly on laser energy
 - irradiance, pulse width
- **Composition (Chemistry) of ablated mass**
 - Composition of ablated mass depends non-linearly on laser energy
 - Composition of ablated mass and sample can be the same using appropriate laser conditions



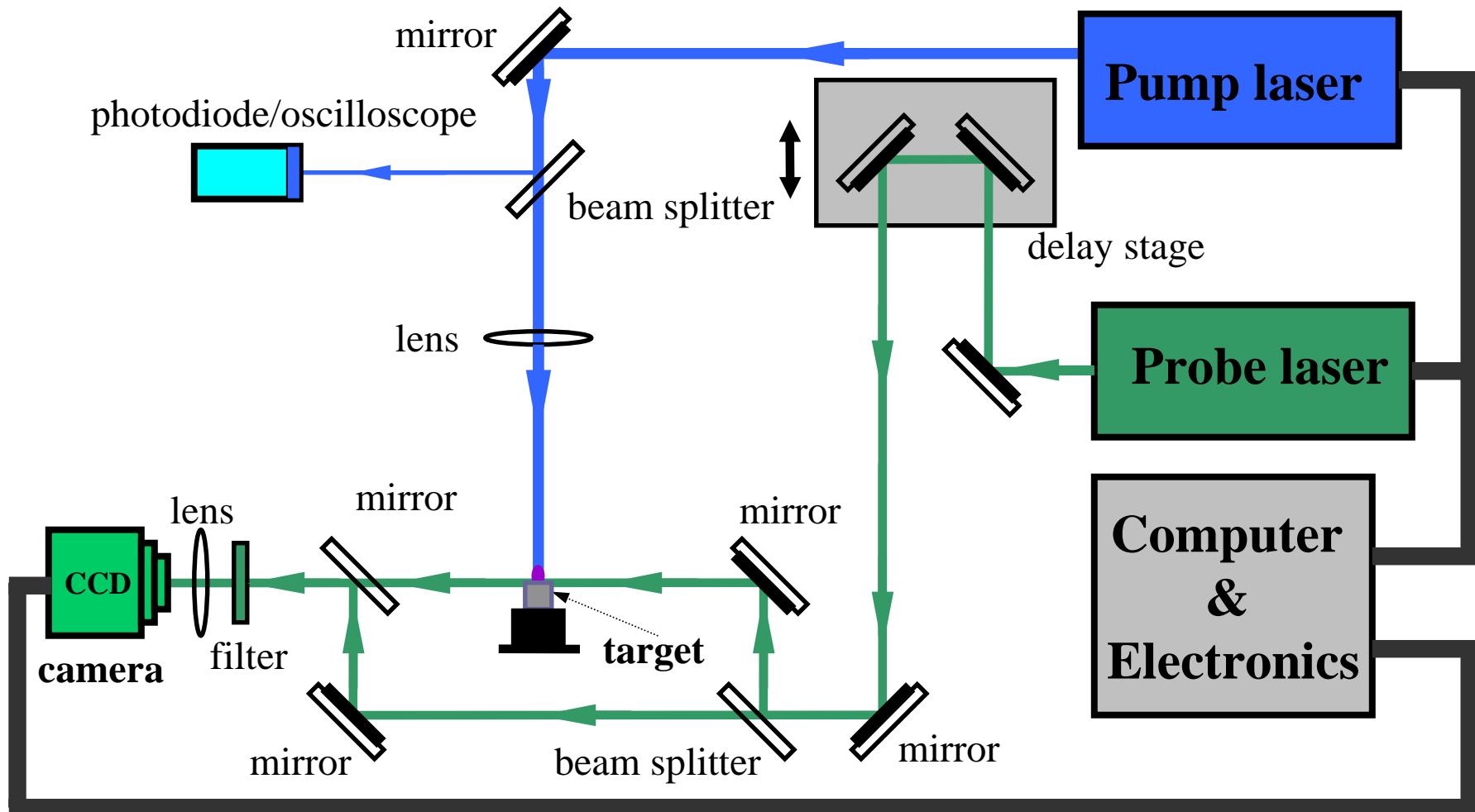


Fundamental Studies of LA Plasmas

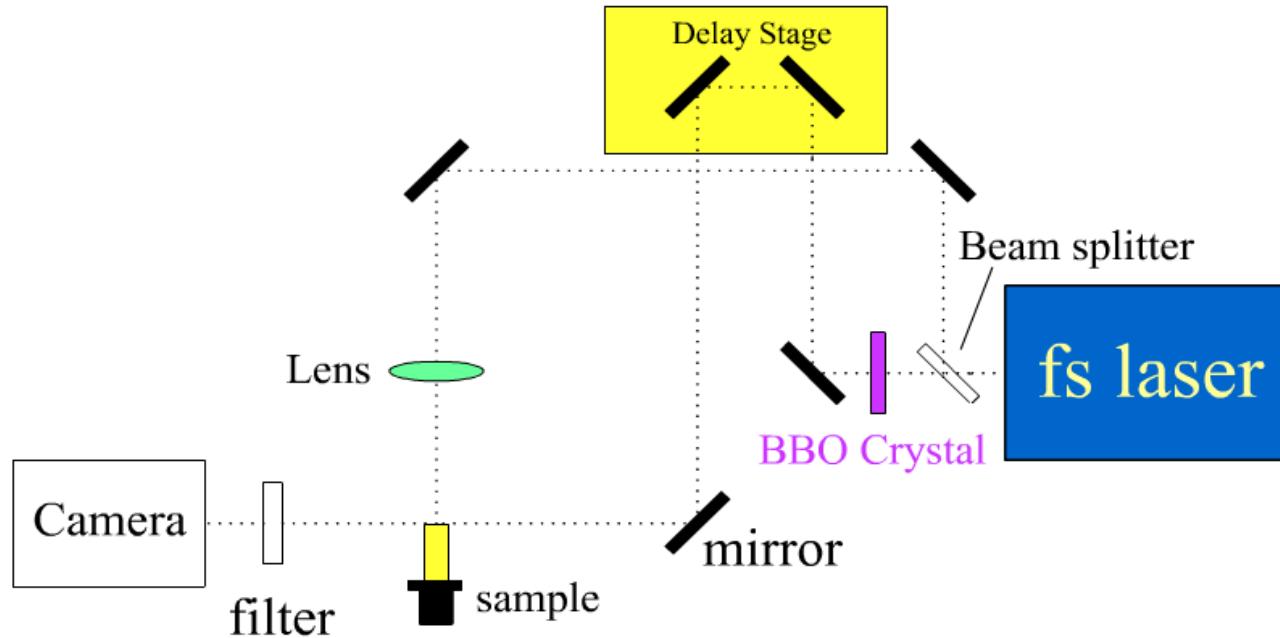
**Time-resolved imaging and
interferometry**

Spectroscopic imaging

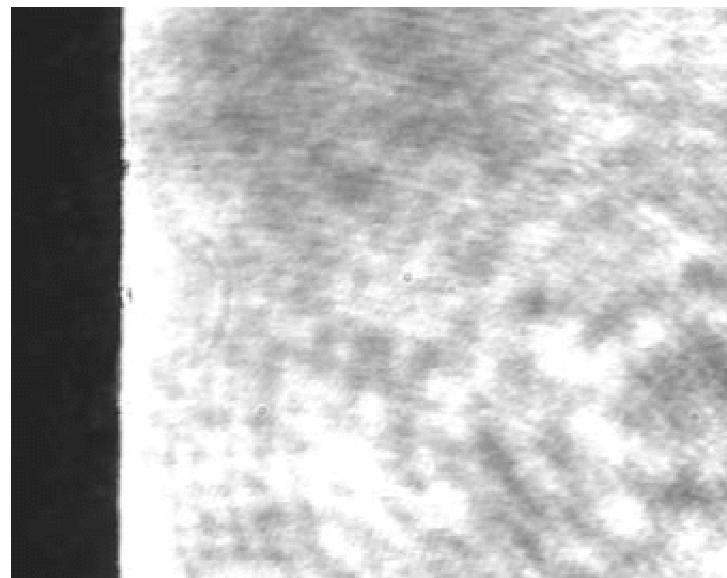
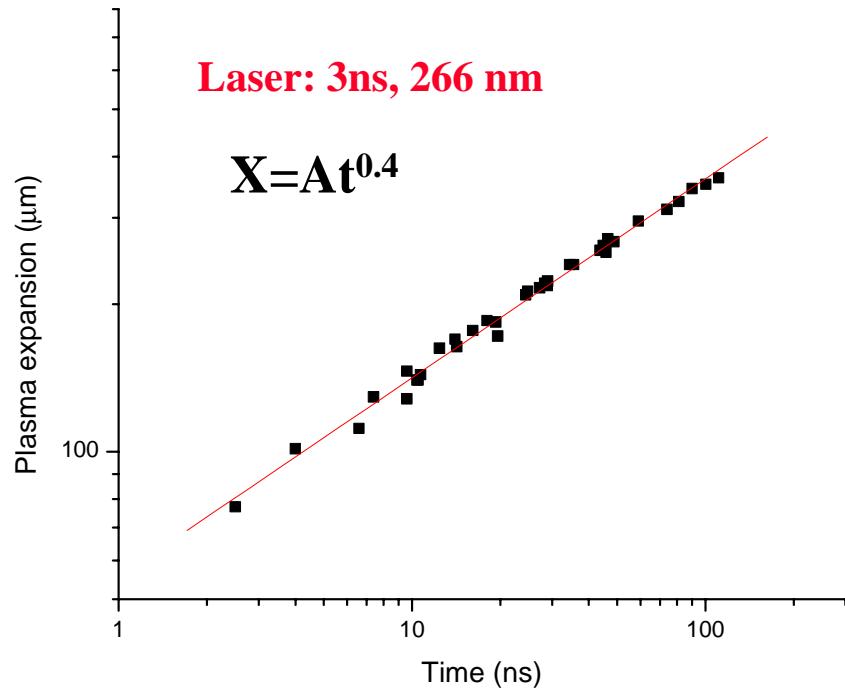
Time-resolved imaging and interferometry



Experimental System pump-probe technique



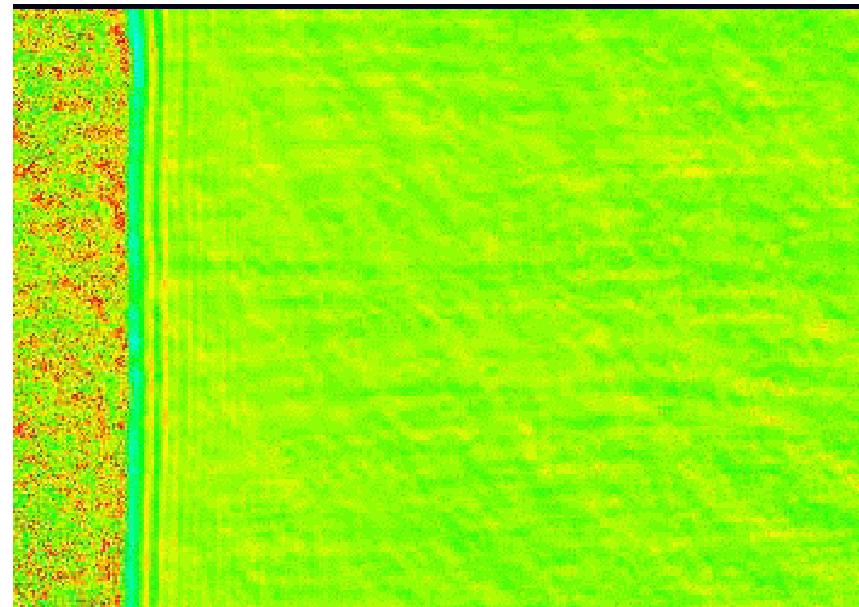
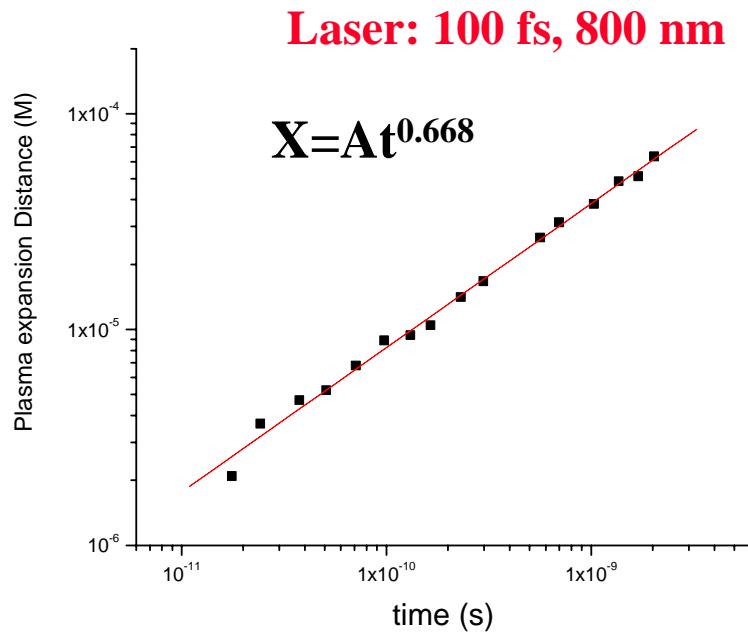
ns plasma expansion



$$X = \lambda_0 \left(\frac{E_0}{\rho} \right)^{1/(2+d)} t^{2/(2+d)}$$

λ_0 unit constant
 ρ air density
d dimensionality = 3

fs plasma expansion



$$X = \lambda_0 \left(\frac{E_0}{\rho} \right)^{\frac{1}{(2+d)}} t^{\frac{2}{(2+d)}}$$

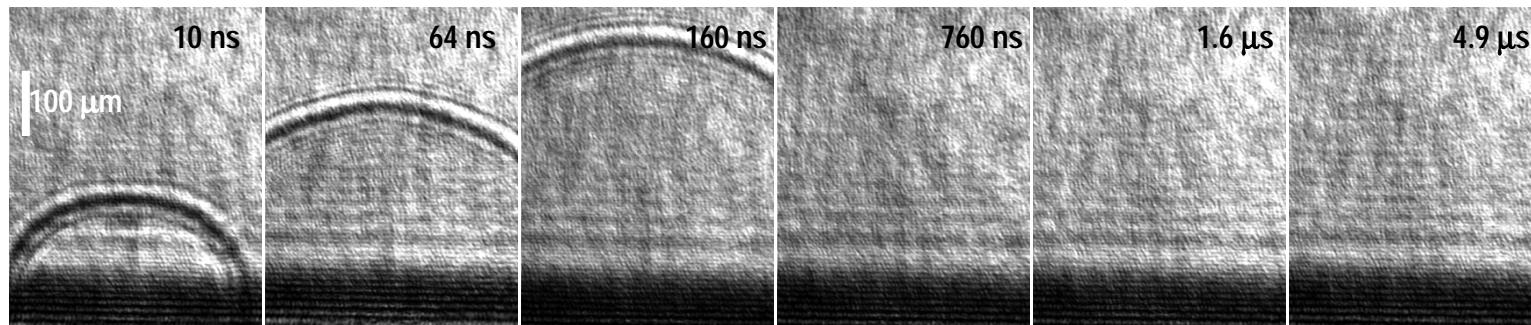
λ_0 unit constant
 ρ air density
d dimensionality = 1

Phase Explosion



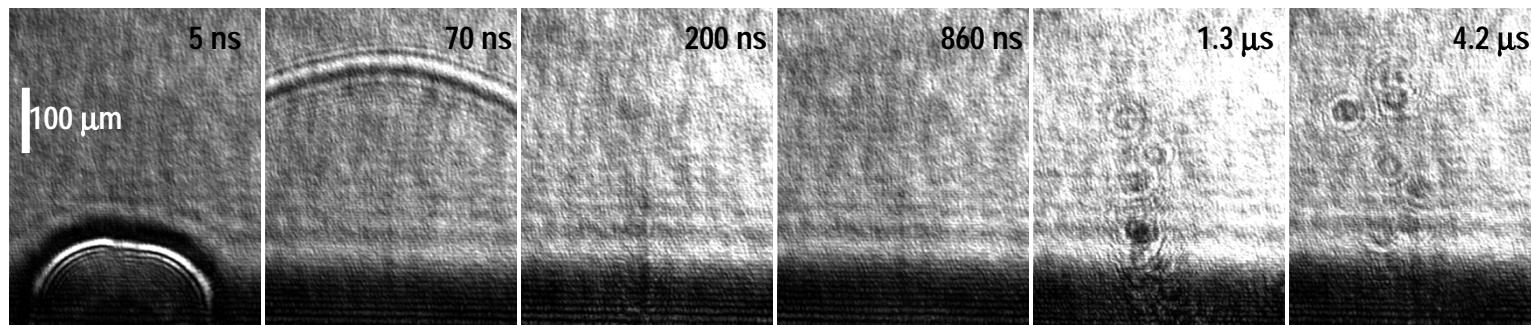
☞ Plume evolution – from nanosecond to microsecond

● below threshold



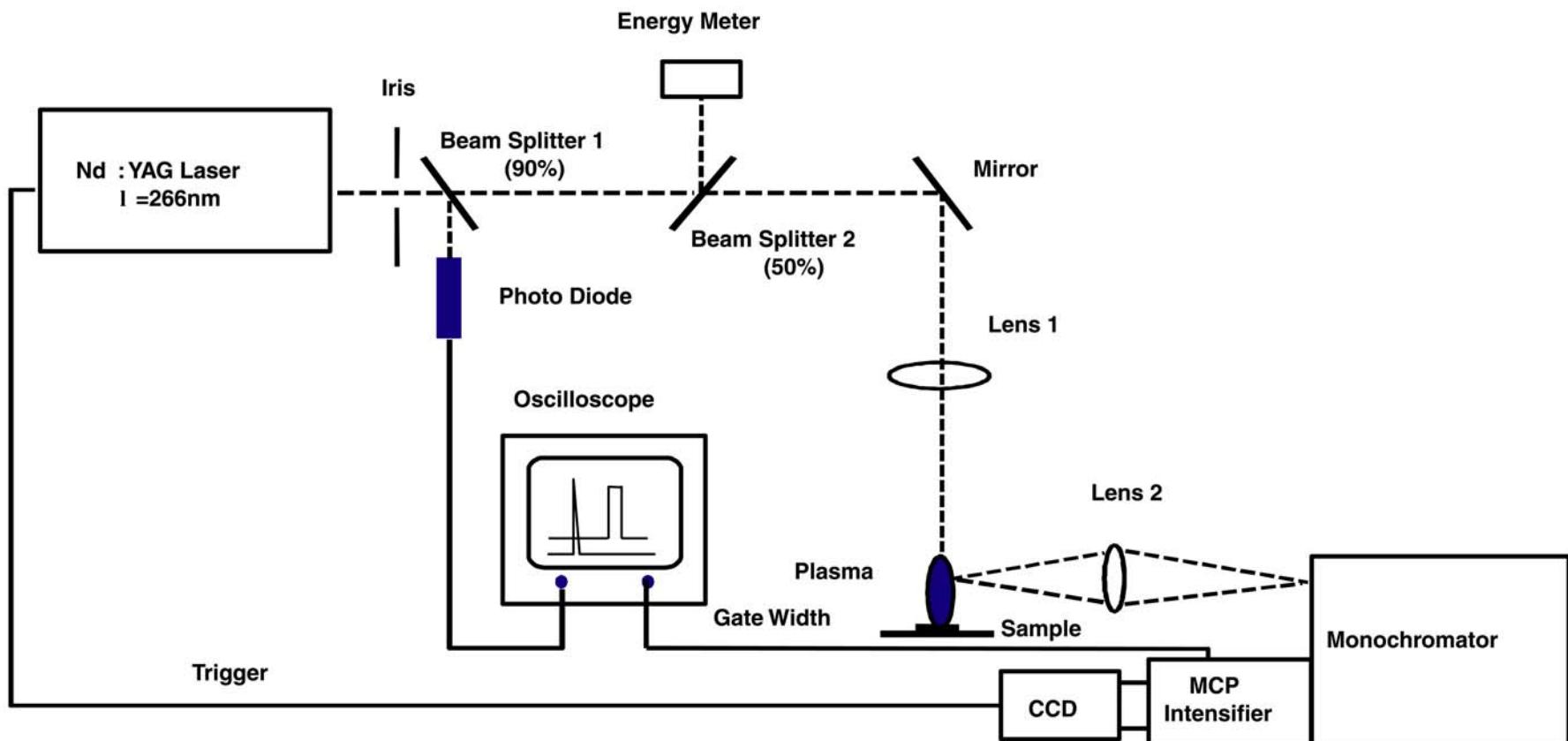
(3 ns, $1.8 \times 10^{10} \text{ W/cm}^2$)

● above threshold

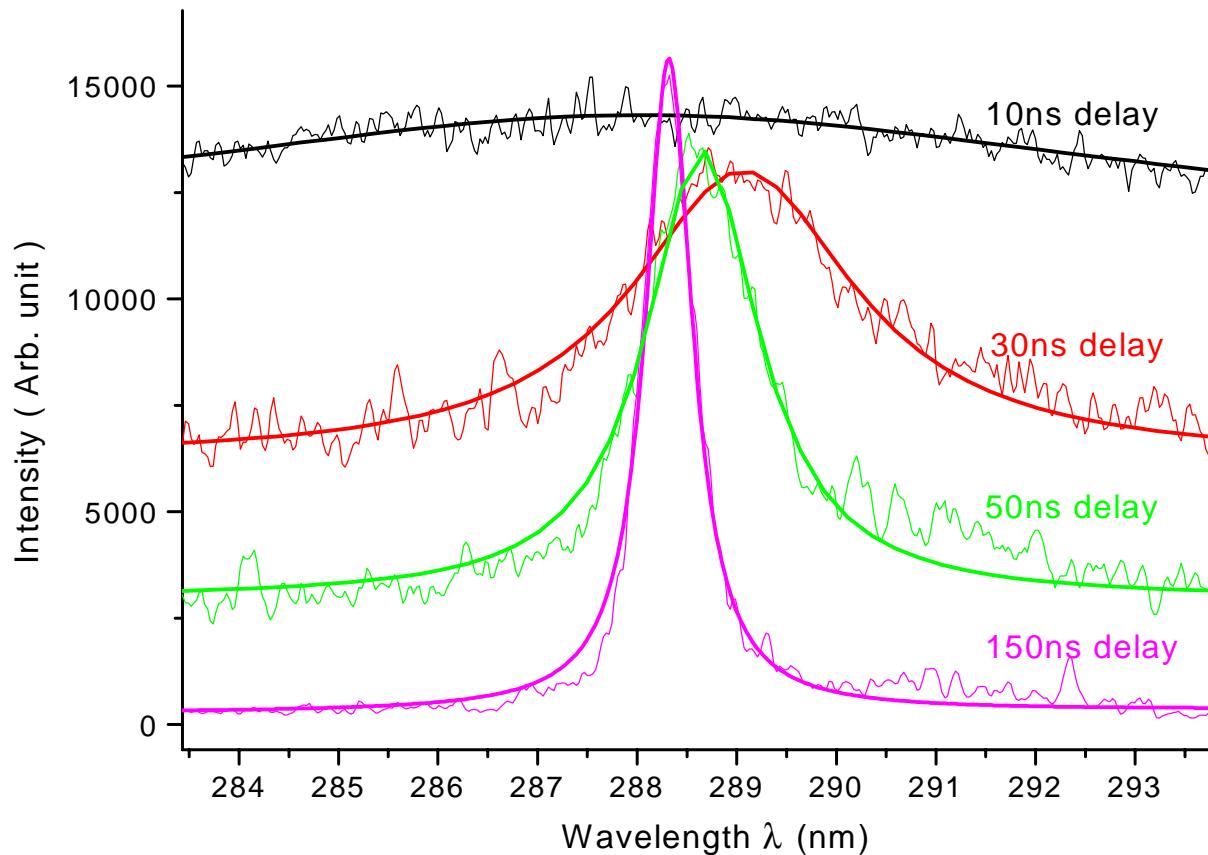


(3 ns, $2.1 \times 10^{10} \text{ W/cm}^2$)

Plasma Spectroscopy (LIBS)



Silicon Emission vs. Delay Time



- Mostly continuum emission at 10 ns delay
- The longer the delay, the narrower is the peak width
- Continuum emission decreases with delay time
- Characteristics of emission related to plasma properties

Spectroscopy



1. Electron number density is calculated from Stark broadened FWHM :

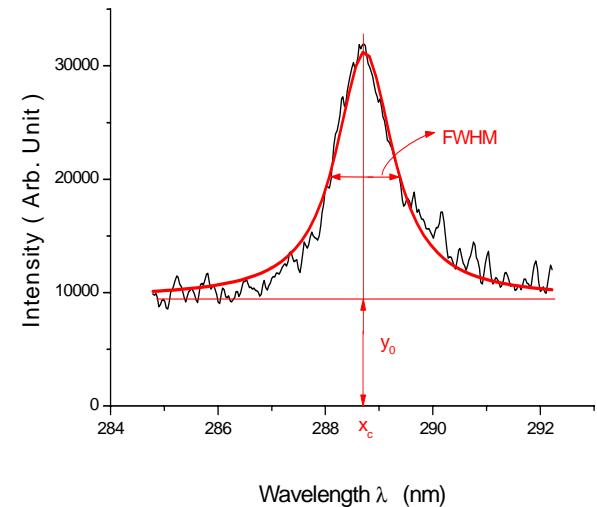
$$\Delta\lambda_{1/2} = 2W \left(\frac{n_e}{10^{16}} \right) \left[1 + 1.75A \left(\frac{n_e}{10^{16}} \right)^{1/4} \left(1 - \frac{3}{4} N_D^{-1/3} \right) \right]$$

2. Plasma temperature is calculated from line and continuum ratio:

$$\frac{\epsilon_l}{\epsilon_c}(\lambda) = C_r \frac{A_{21}g_2}{U_i} \frac{\lambda_c^2}{\lambda_l T_e} \frac{\exp\left(\frac{E_i - E_2 - \Delta E_i}{kT_e}\right)}{\left[\xi\left(1 - \exp\frac{-hc}{\lambda kT_e}\right) + G\left(\exp\frac{-hc}{\lambda kT_e}\right)\right]}$$

Stark broadened line profile and Lorentzian fitting:

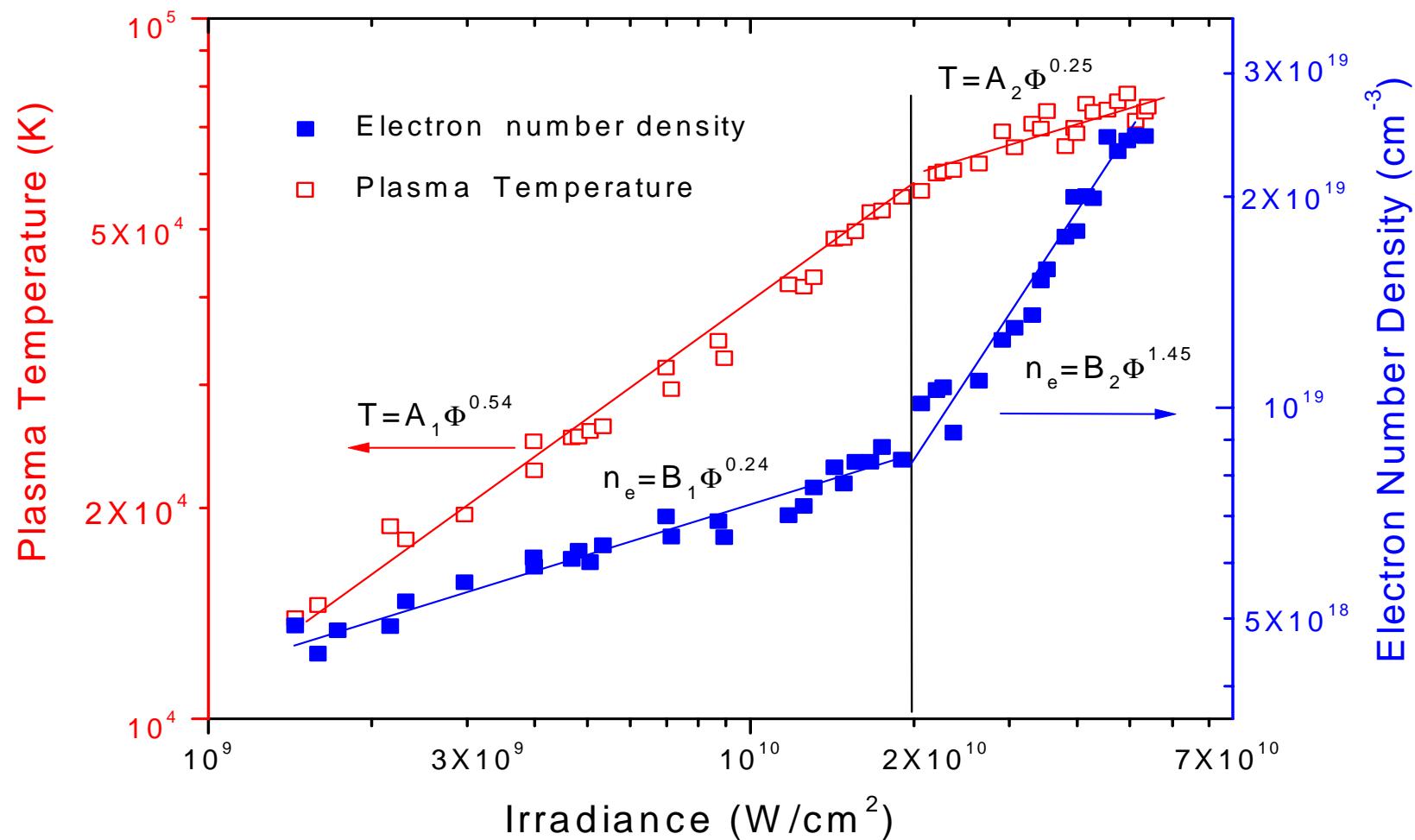
$$y = y_0 + \frac{2A}{\pi} \frac{\Delta\lambda_{1/2}}{4(x - x_c) + \Delta\lambda_{1/2}^2}$$



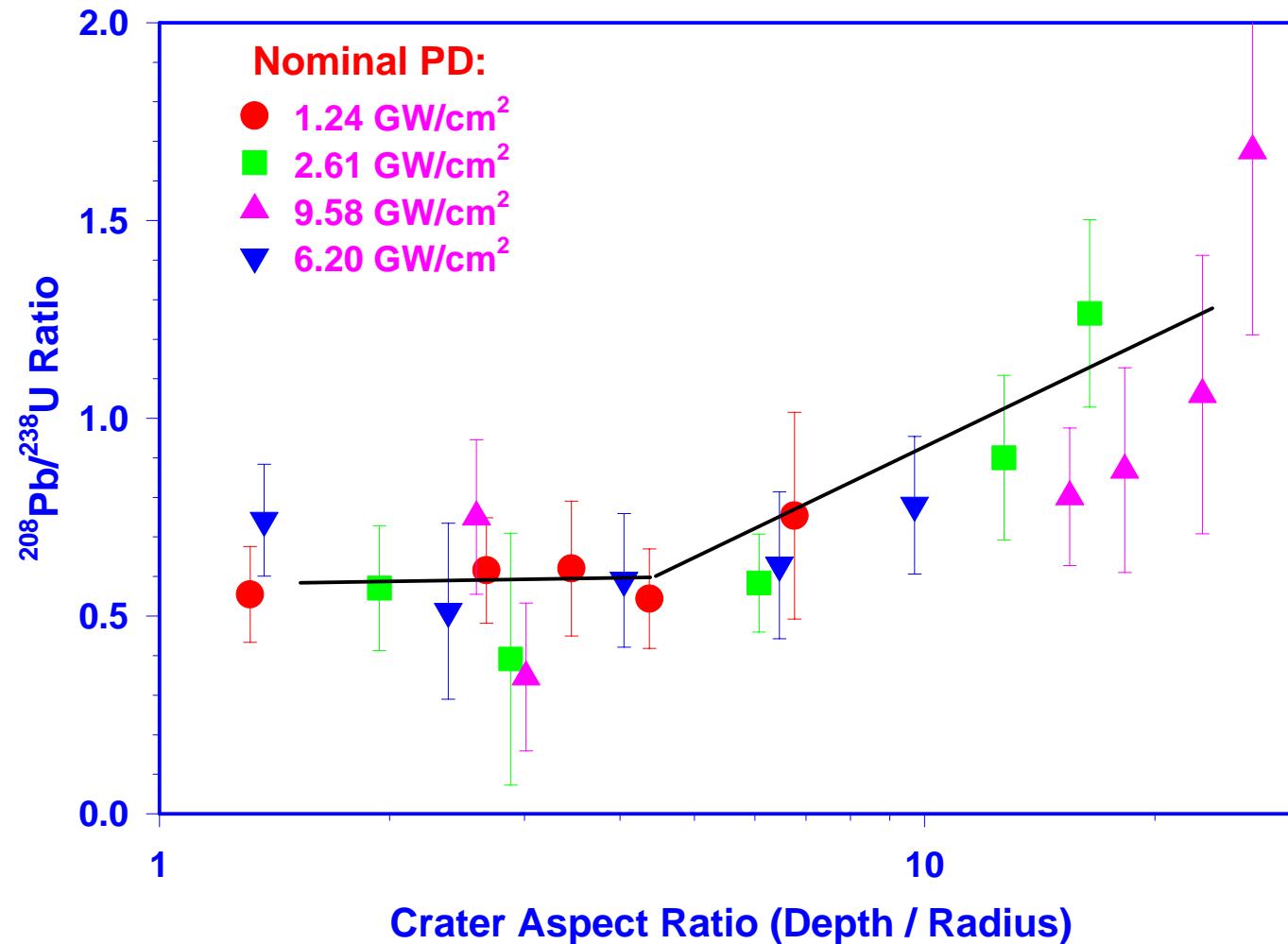
Plasma Temperature and Electron Density



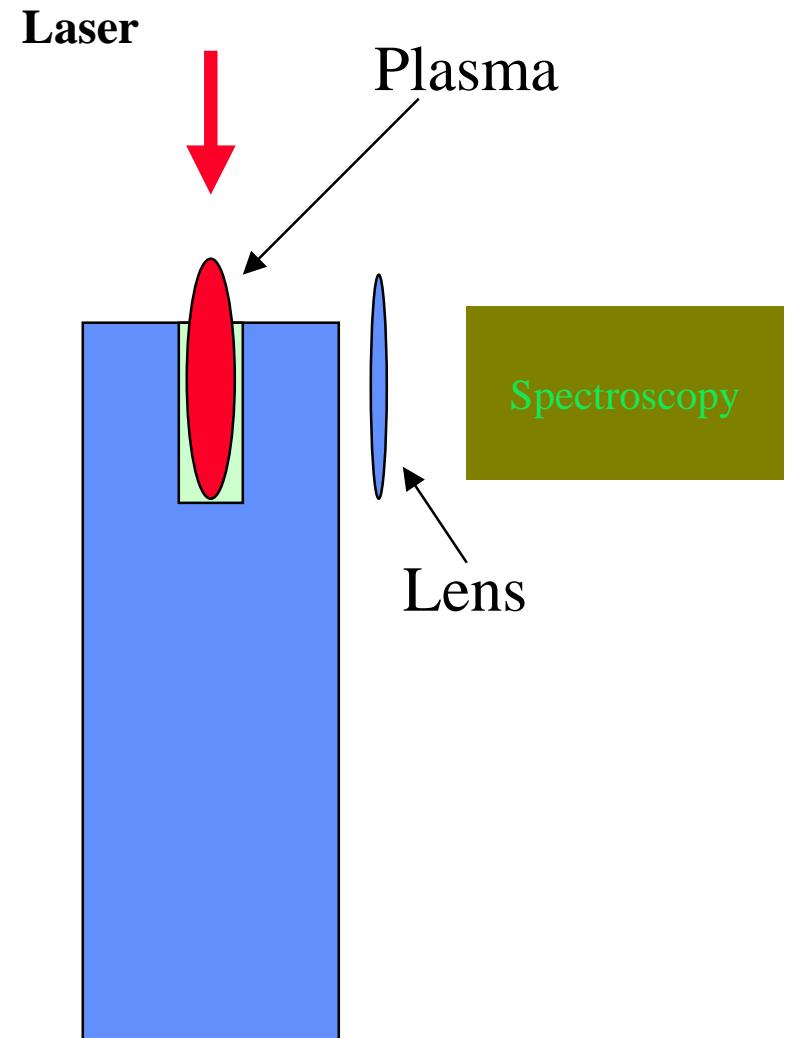
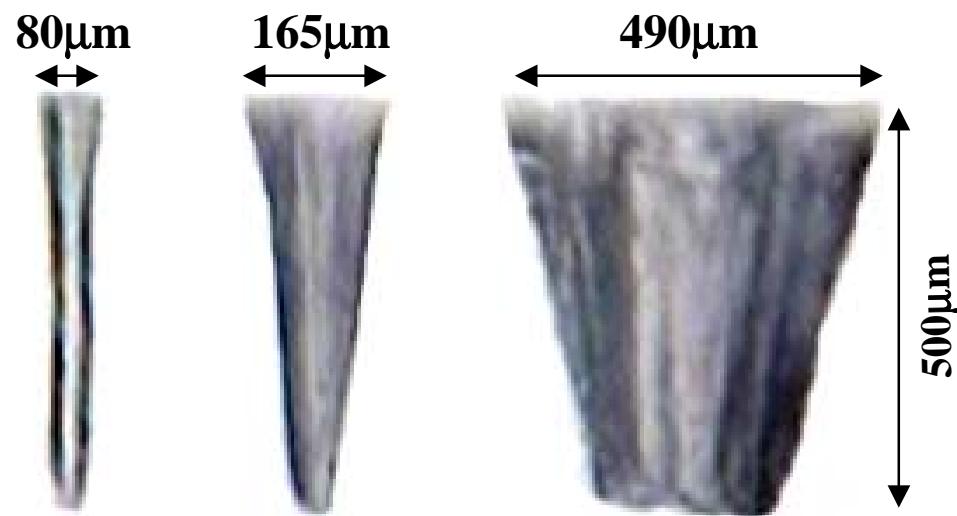
Nd: YAG Laser, $\lambda=266\text{nm}$, $t_p=3\text{ns}$, $t_d=30\text{ns}$, $t_g=20\text{ns}$



Fractionation vs. Crater Aspect Ratio

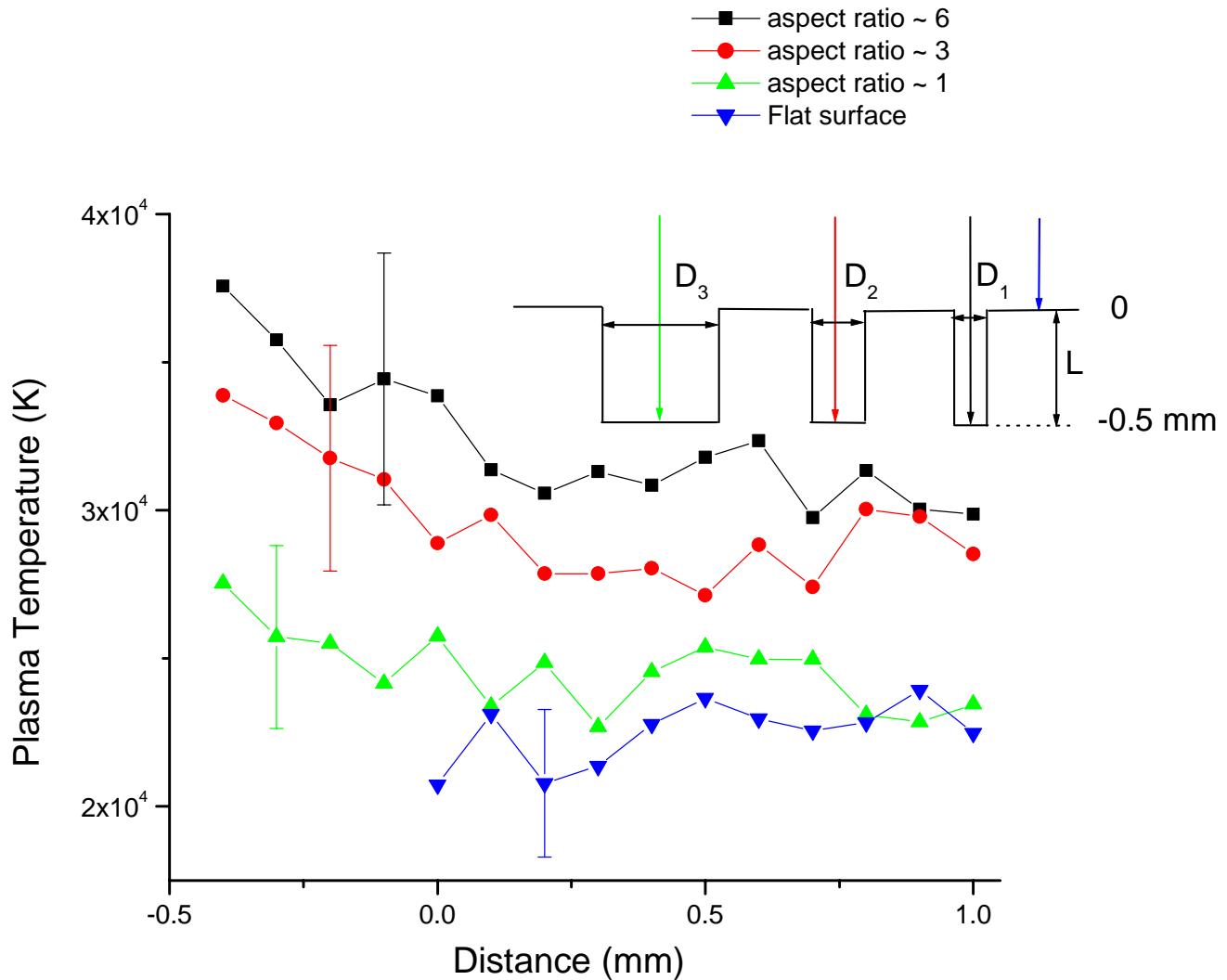


Laser-drilled crater



Craters laser drilled in edge of Fused Silica

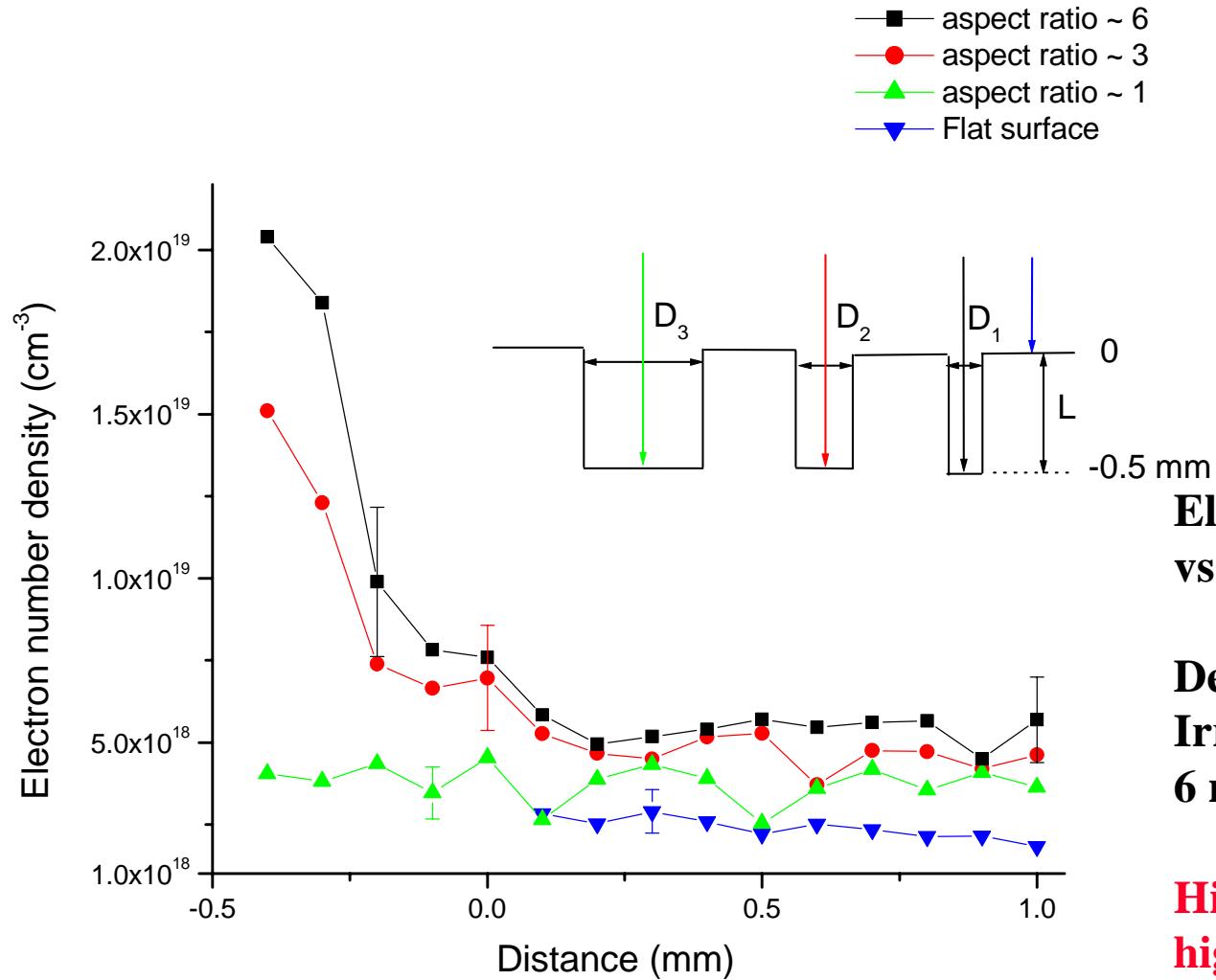
Temperature vs. Distance



Plasma temperature vs. distance from 'surface'.

Delay time = 100 ns
Irradiance = 6.95
GW/cm²
6 ns pulse, 266nm

Electron Density vs. Distance

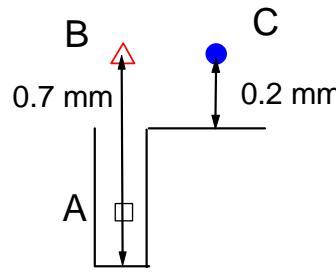
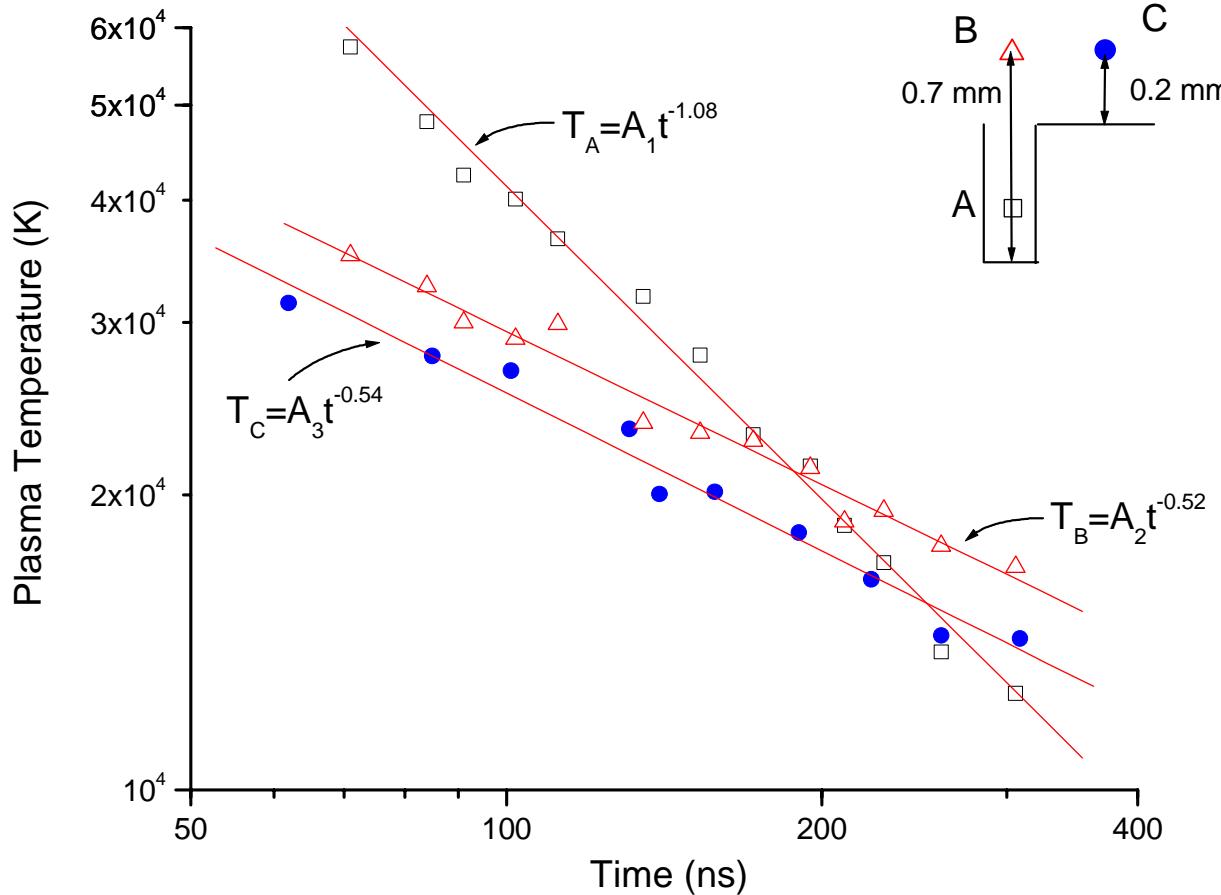


Electron number density
vs. distance from ‘surface’

Delay time = 100 ns
Irradiance = 6.95 GW/cm
6 ns pulse, 266nm

**Higher aspect ratio =
higher temperature and
electron number density**

Plasma expansion



Temporal evolution of plasma temperature inside and outside of the cavity.

Cavity diameter is 80 micron and depth 480 micron. Irradiance is 7.67 GW/cm².



Femtosecond Ablation

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Laser Material Interactions



ns pulsed laser ablation

Large heat-effected zone
Laser-plasma interaction
Ejection of large melted particles



fs pulsed laser ablation

Nominal heat-effected zone
No laser-plasma interaction
Condensation of smaller particles



Laser-induced Plasma Images



Photographs of laser explosion at a copper sample surface

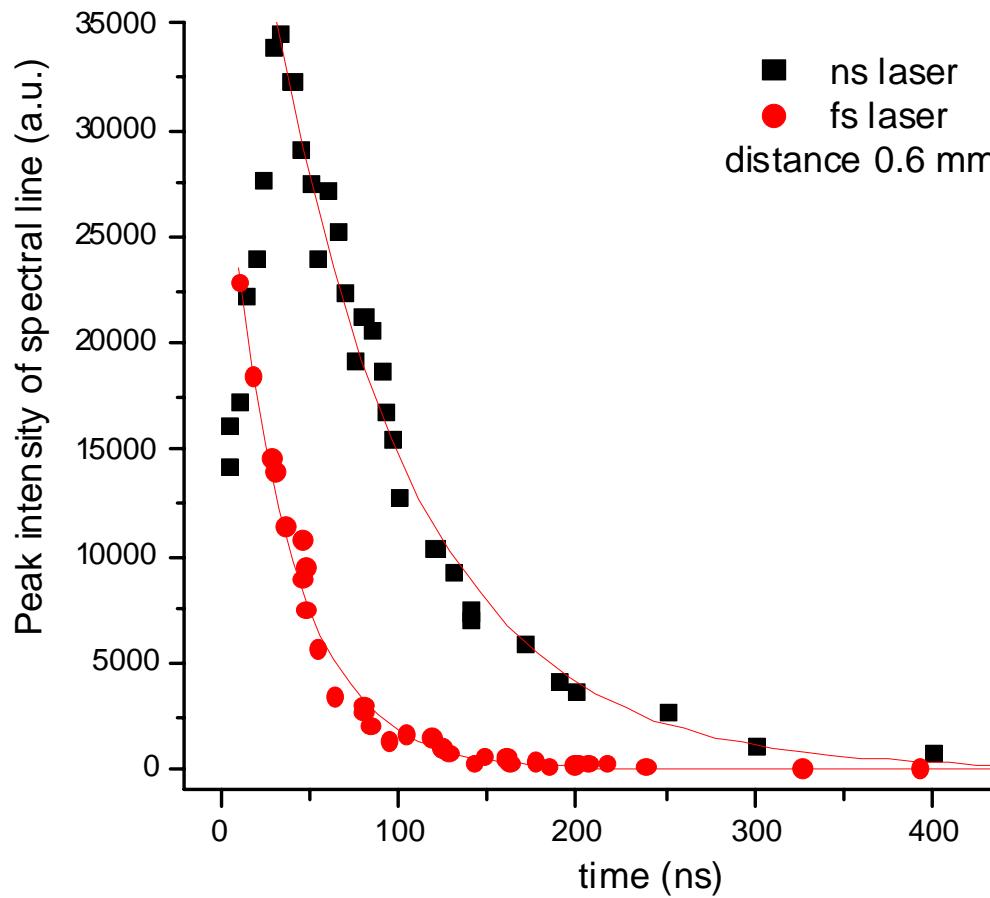
Nanosecond:
Laser plasma interaction
Significant plasma influence on sampling



Femtosecond:
No laser plasma interaction
Reduced plasma influence on sampling



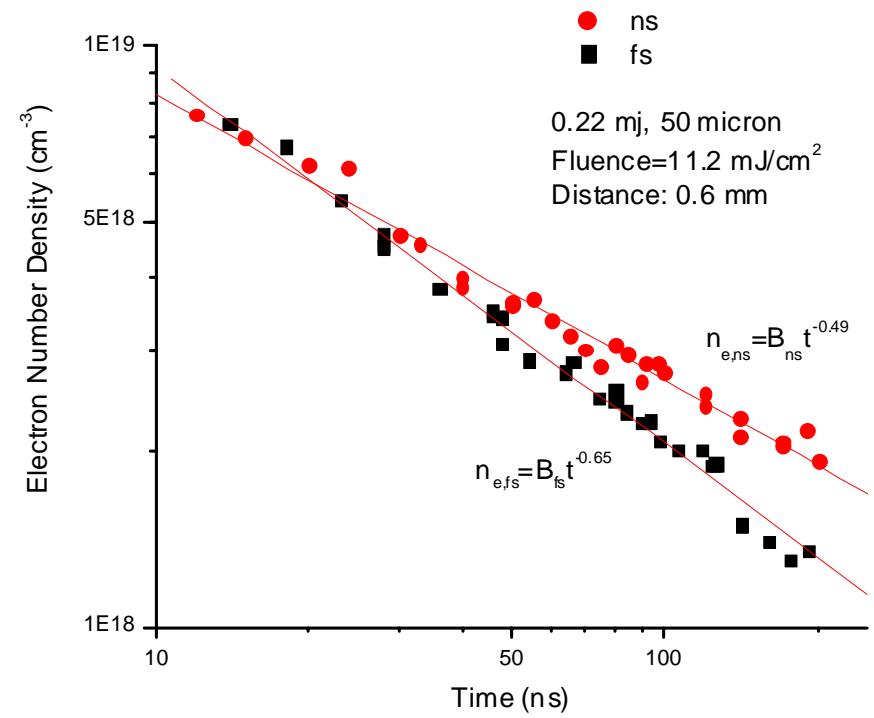
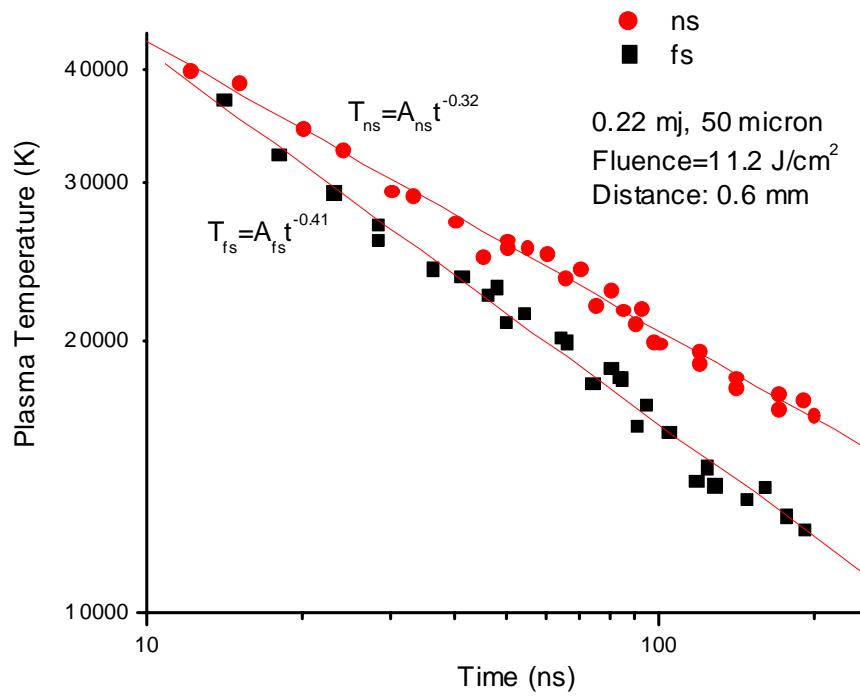
Laser Induced Plasma Emission Intensity



Same wavelength,
energy and spot size

Higher intensity and
longer lifetime for ns
plasma due to laser-
plasma interaction.

Plasma temperature and density

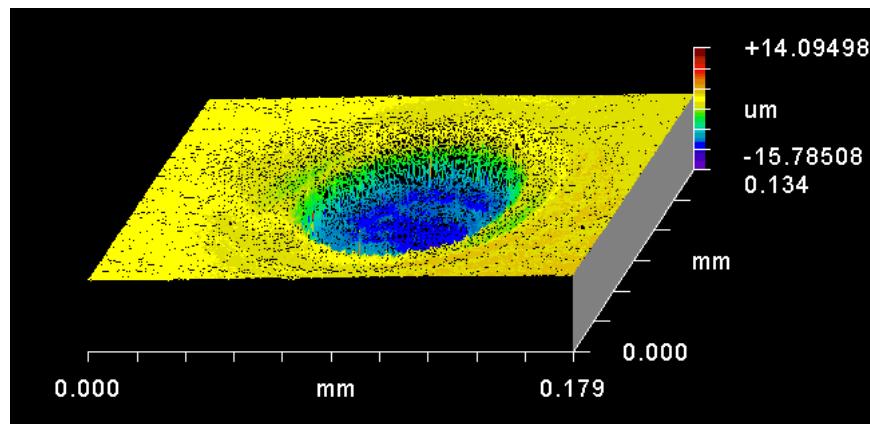


Temperature and number density of plasma decrease faster for fs than ns laser
cooling effects on particles?

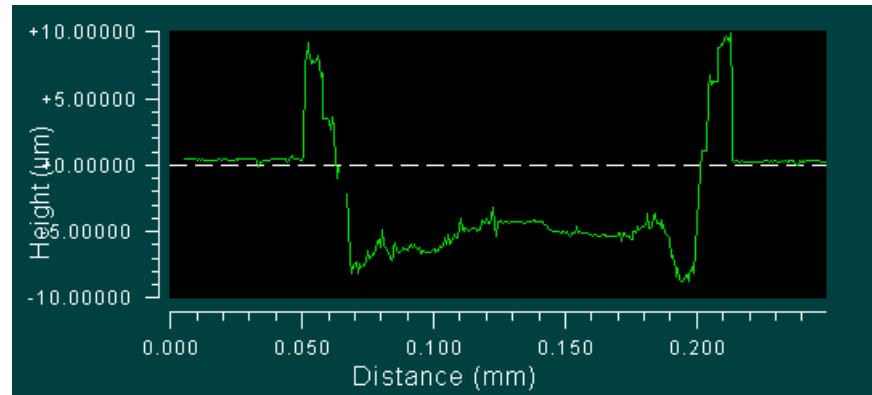
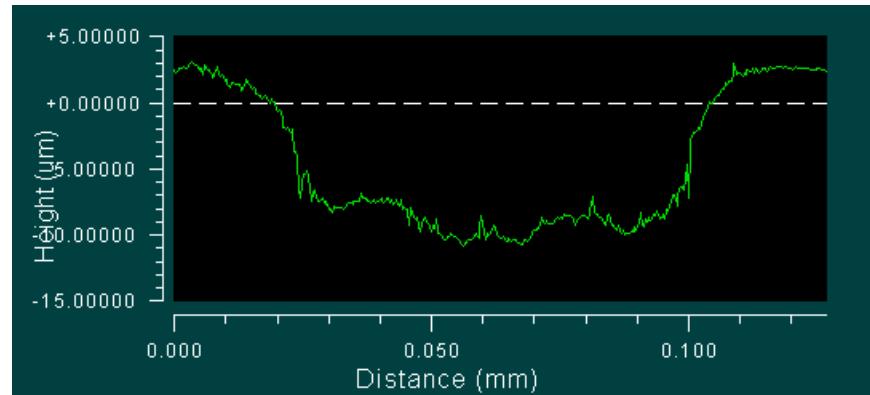
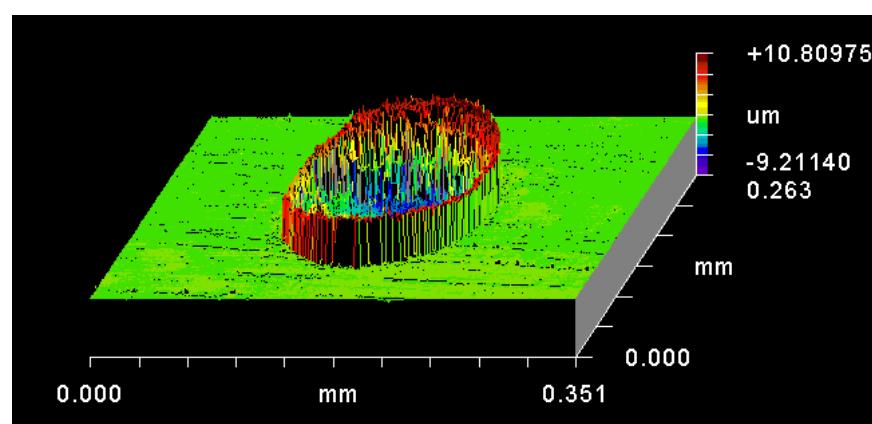
Craters in Brass Sample (40 pulses)



150 fs



6 ns



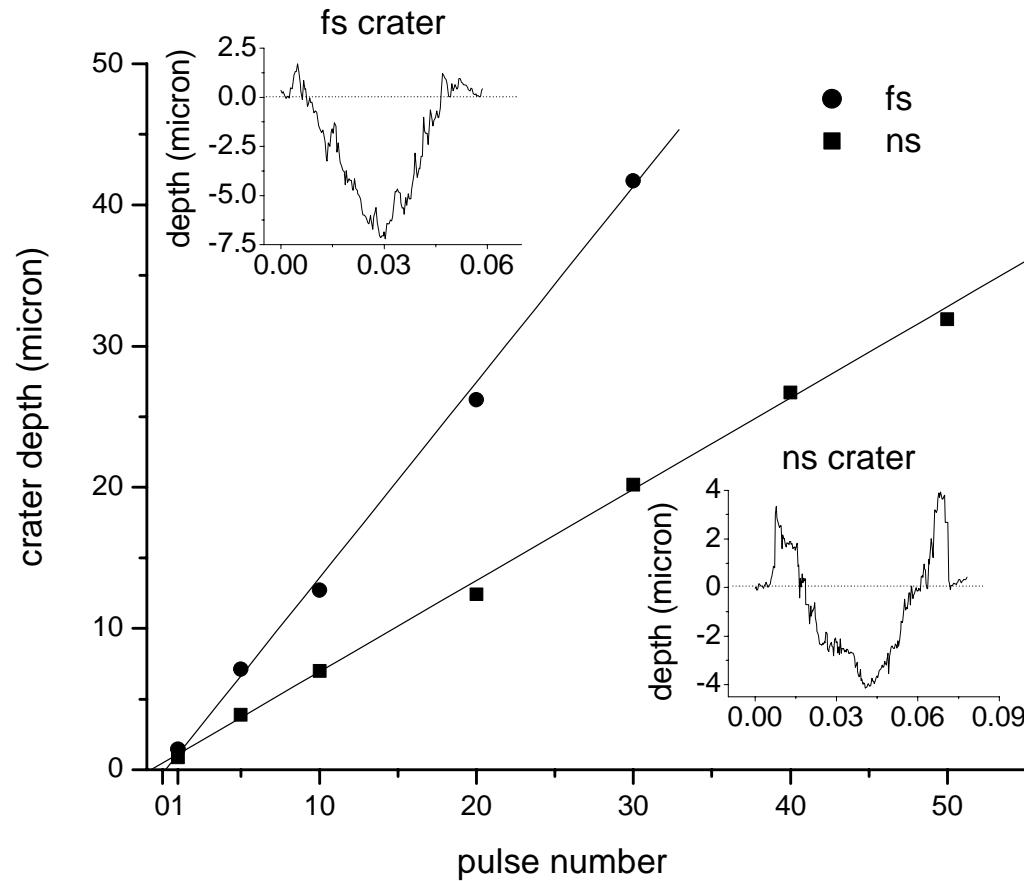
Ablation rate – quantity of mass/pulse



NIST 610

Same laser
fluence and
wavelength

Higher mass
ablation rate
with fs ablation.

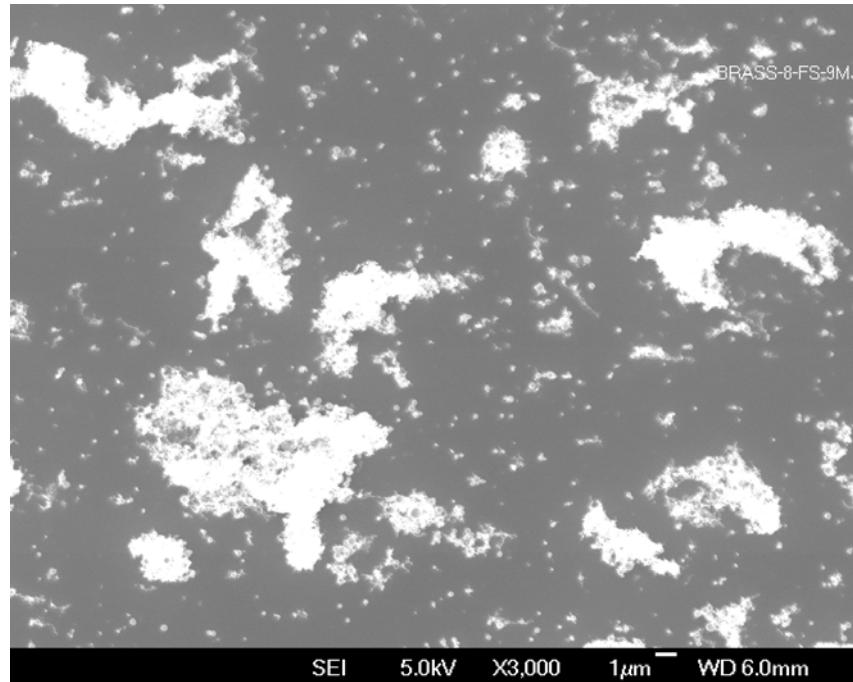


Scanning Electron Microscopy

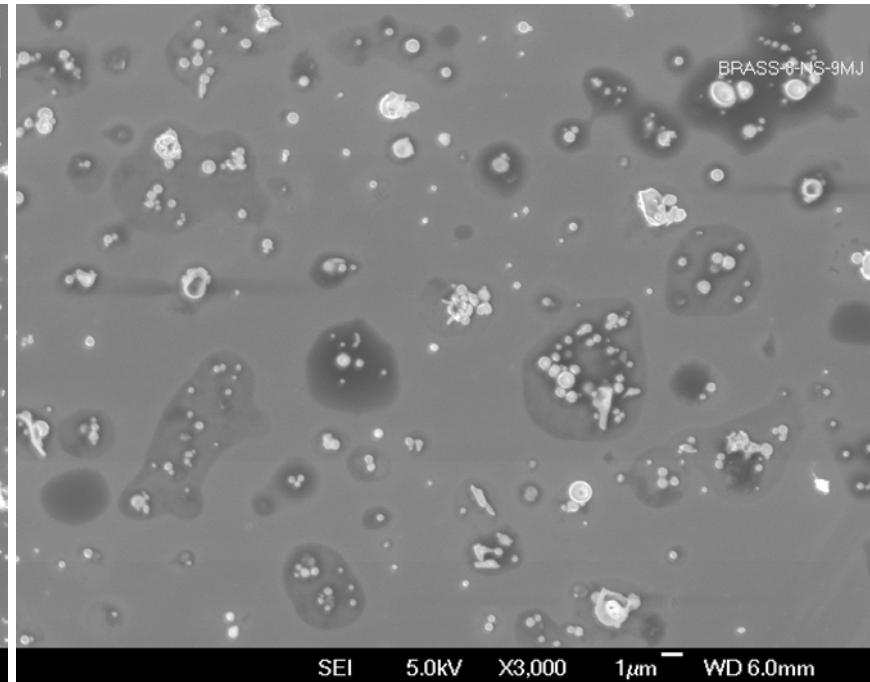


Particles collected at exit of ablation chamber –
significant difference in particle size and morphology!

Brass (Cu 85.1%, Zn 14.9%)



fs laser

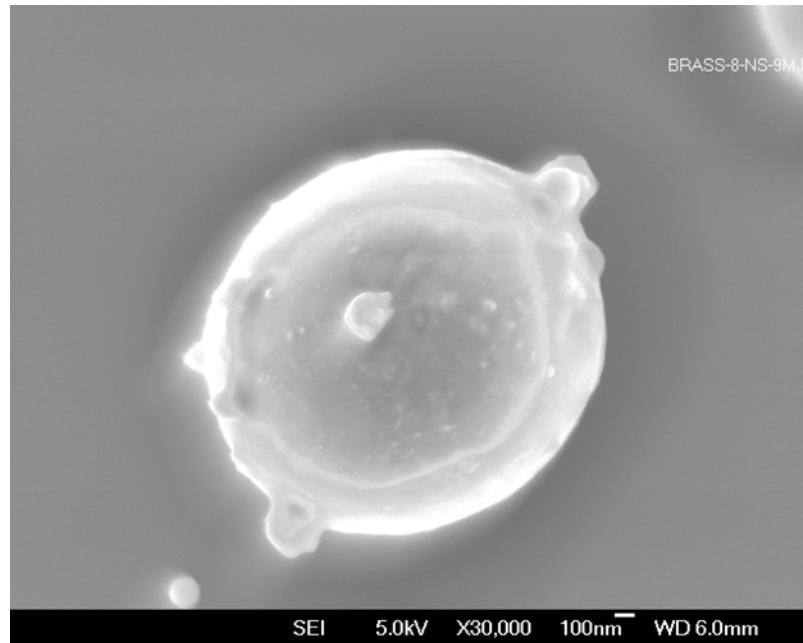
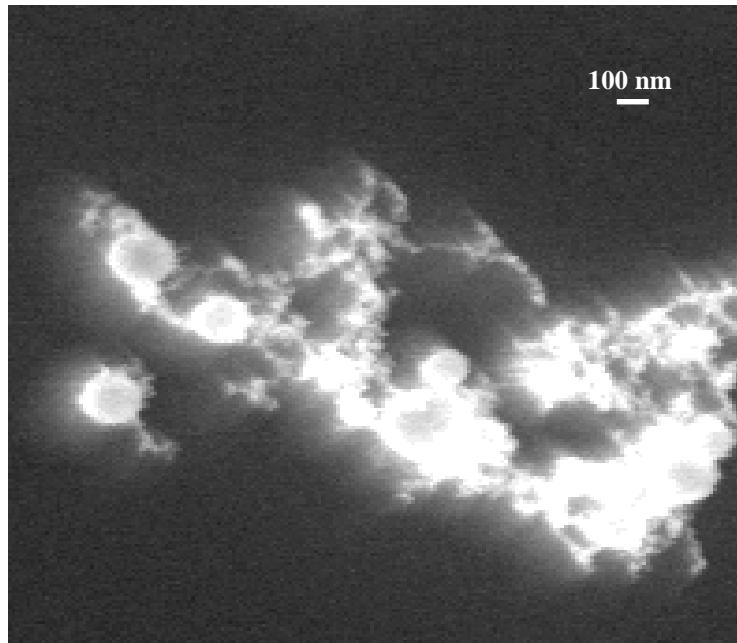


ns laser

Scanning Electron Microscopy



ablated brass particles – SEM 10x from previous slide

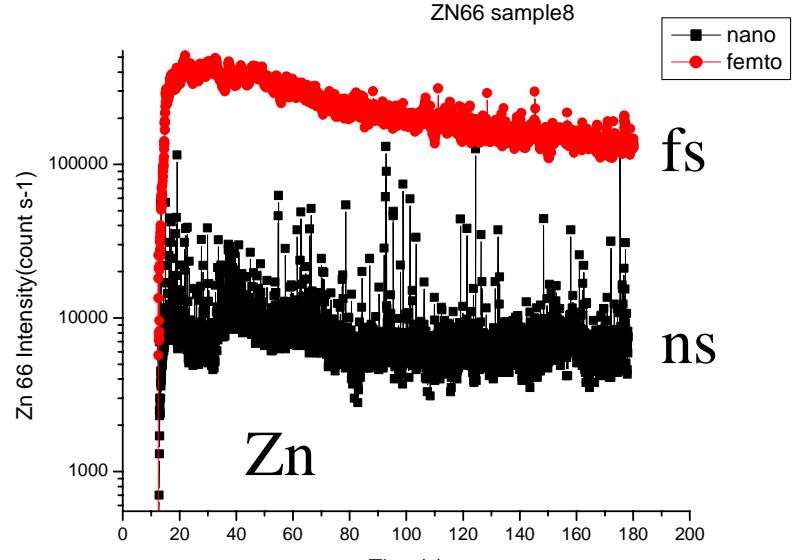
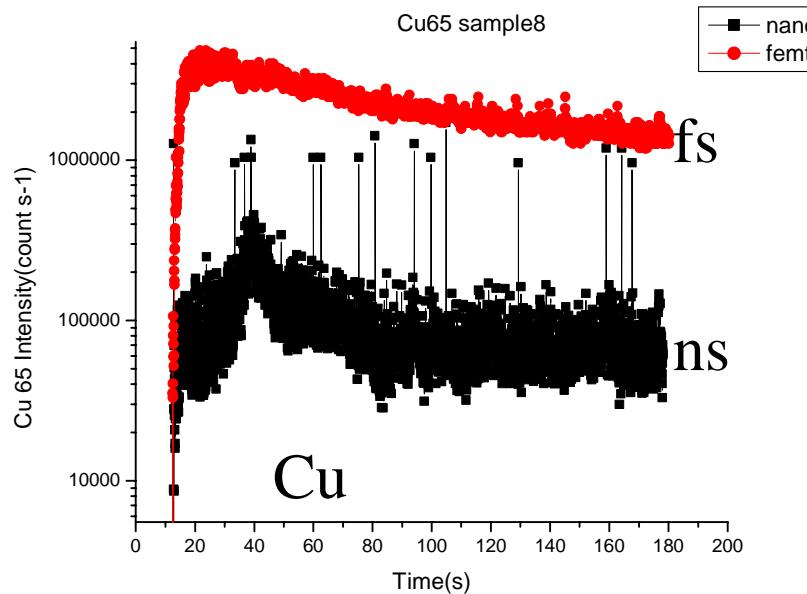


Majority of mass ablated (particle diameter):
fs laser ablation < 250nm
ns laser ablation > 750nm



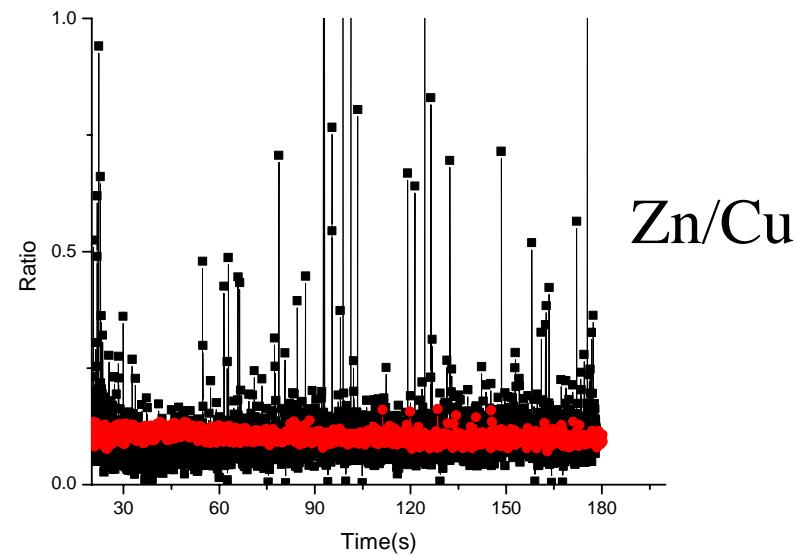
Femtosecond Laser Ablation ICPMS

Ablation – Brass Sample

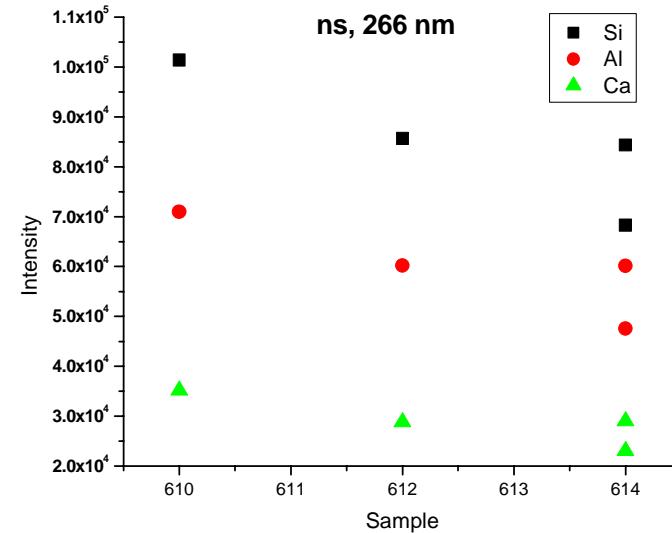
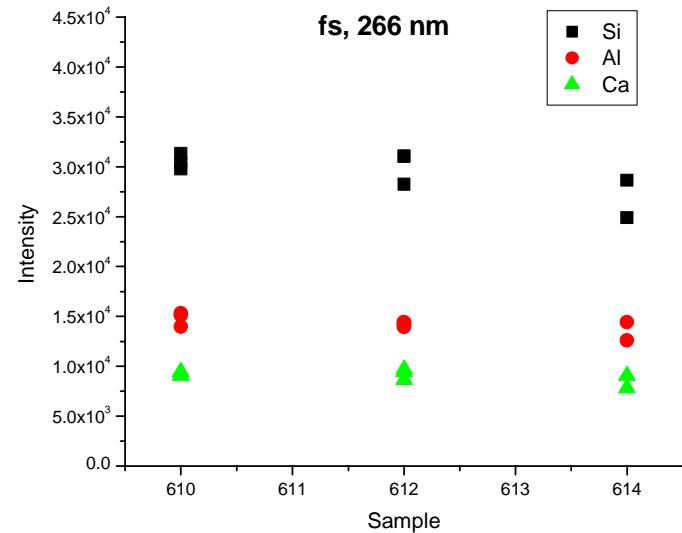


Same wavelength, energy
and spot size

>10X increase in intensity
Fewer spikes in the ICP response
Improved RSD



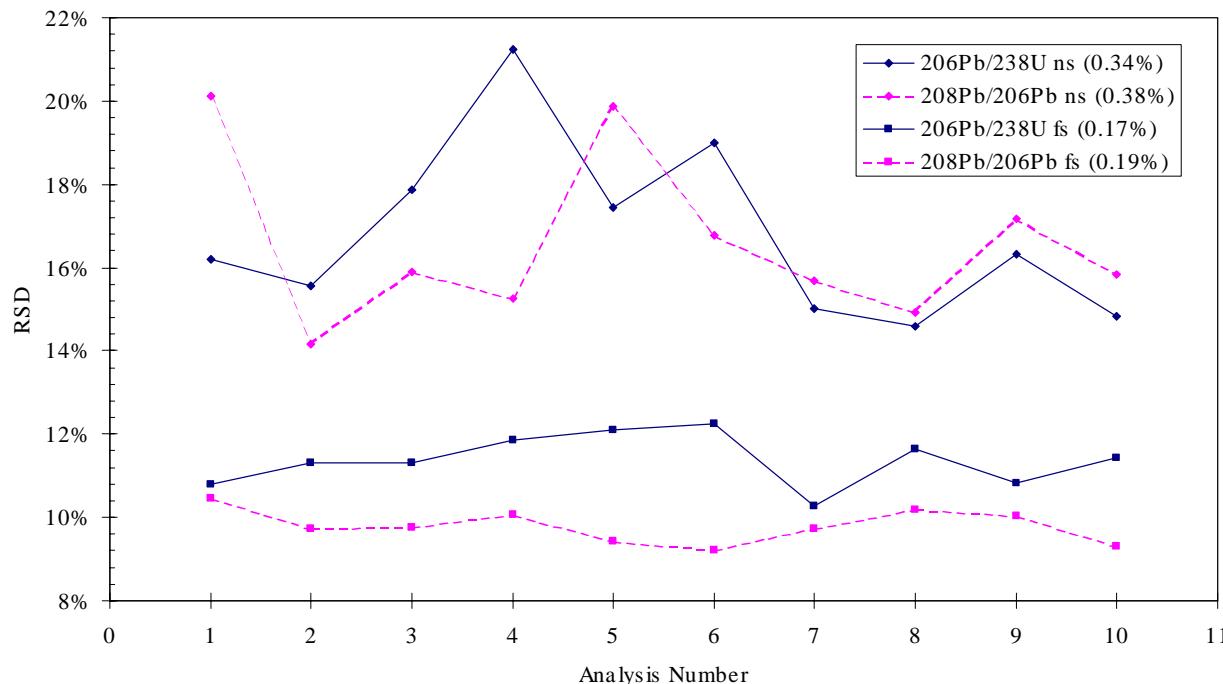
NIST Silicate Glasses



Si, Al and Ca have the same concentration in each NIST sample – ideal case would be to laser ablate the same quantity from each sample and measure the same concentration

Improved matrix independence (for glasses) using femtosecond laser

ICPMS Precision



Sample: NIST 610
Wavelength = 266nm
Equal fluence

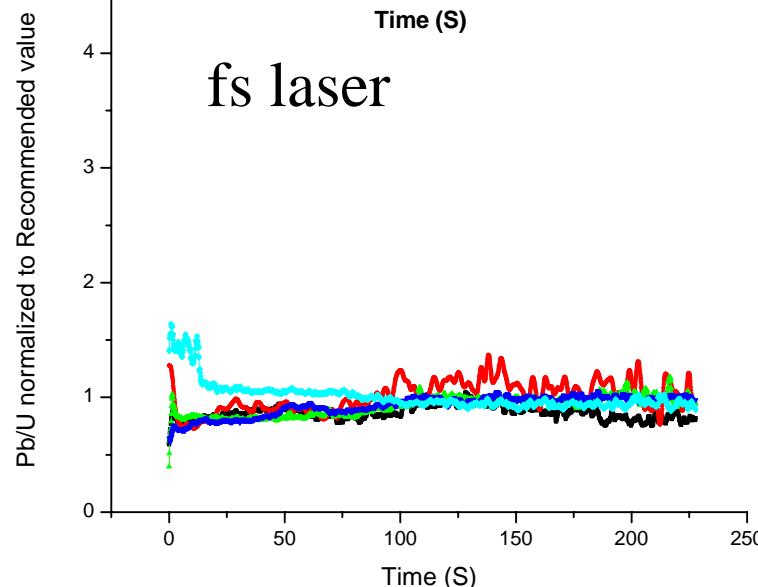
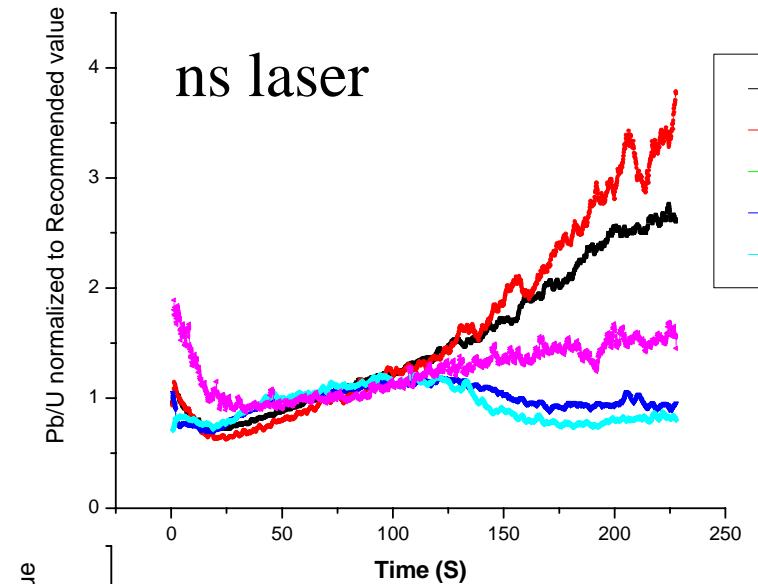
**ns laser – 2% RSD pp
(relative standard deviation)**

fs laser – 5% RSD pp

Each data point represents integrated signal intensity during repetitive sampling at a single sample spot. Analysis number represents different sample spot.

fs laser with poorer peak to peak stability provides better sampling (ablation) precision!

Fractionation



Classic nanosecond-induced fractionation versus crater formation – Pb/U ratio changes as crater is formed!

Ideal = constant ratio!

Significantly reduced matrix and fractionation effects using fs laser ablation!

Accuracy

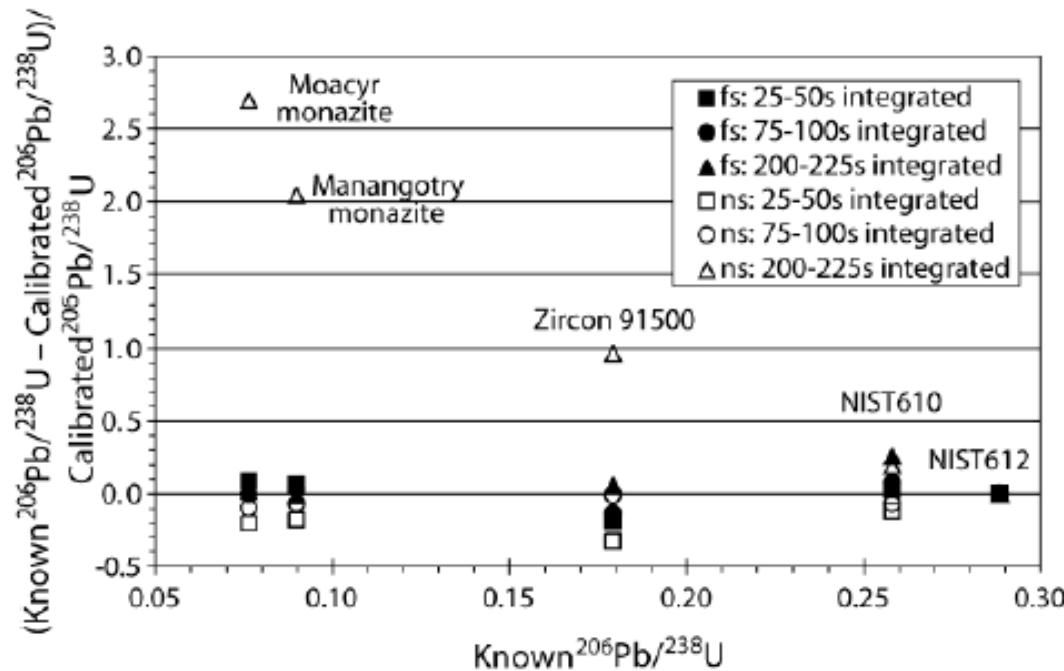


Figure 7. Known atomic $^{206}\text{Pb}/^{238}\text{U}$ ratios on NIST610 and 612 standard glasses, zircon 91500, and Manangotry and Moacyr monazites, against the relative difference between these known values and the calibrated values (to NIST612) obtained in this study. The results are shown for different integration time periods after the start of ablation for both nanosecond and femtosecond lasers. Accuracy of femtosecond data is much less sensitive to the integration time slice chosen for the calculation.

Poirrasson F. Mao XL. Mao SS. Freydier R. Russo RE. Comparison of ultraviolet femtosecond and nanosecond laser ablation inductively coupled plasma mass spectrometry analysis in glass, monazite, and zircon. Analytical Chemistry. 75(22):6184-6190, 2003.



Future

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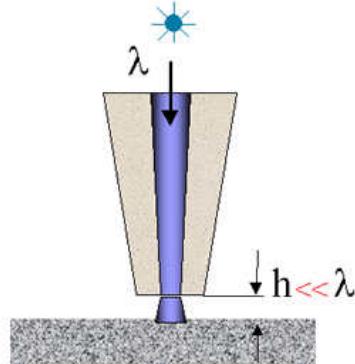
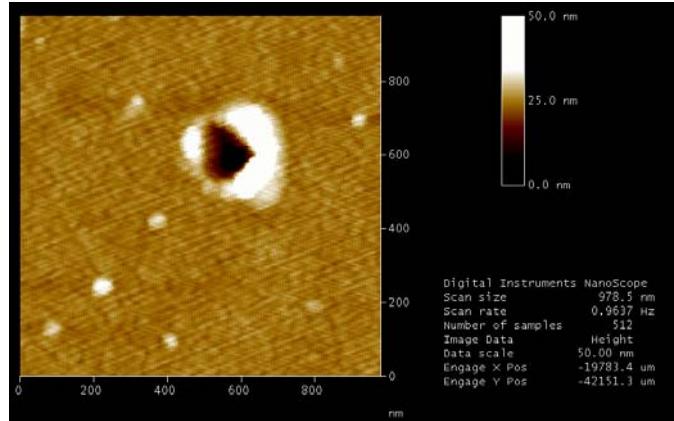
Nano Ablation



AFM tip interaction
Silicon sample

Diameter = 80nm

Spatial resolution in a single particle
Grain boundaries in a crystal



Nearfield imaging

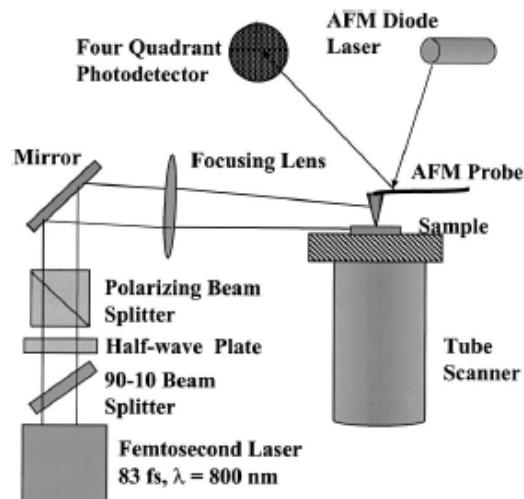


FIG. 1. Schematic diagram of experimental setup.

Nanoscale Atmospheric Pressure Laser Ablation-Mass Spectrometry, Raoul Stockle, Patrick Setz, Volker Deckert, Thomas Lippert, Alexander Wokaun, and Renato Zenobi, Anal. Chem. 2001, 73, 1399-1402

Looking at the nanoscale: scanning near-field optical microscopy, M. De Serio, R. Zenobi, V. Deckert

Trends in Analytical Chemistry, Vol. 22, No. 2, 2003

Topographical and Chemical Microanalysis of Surfaces with a Scanning Probe Microscope and Laser-Induced Breakdown Spectroscopy, Dmitri Kossakovski and J. L. Beauchamp, Anal. Chem., 2000, 72, 4731-4737

Martian Ablation



The smooth surfaces of angular and rounded rocks seen in this image of the martian terrain released by NASA Tuesday Jan. 6, 2004 may be the result of ~~wind polishing debris~~ laser ablation. The picture was taken by the panoramic camera on the Mars Exploration Rover Spirit. NASA unveiled a breathtaking color photo of the surface of Mars, the sharpest photograph ever taken on the surface of Mars. NASA scientists called the picture a 'postcard,' sent across 105 million miles of space to Earth.

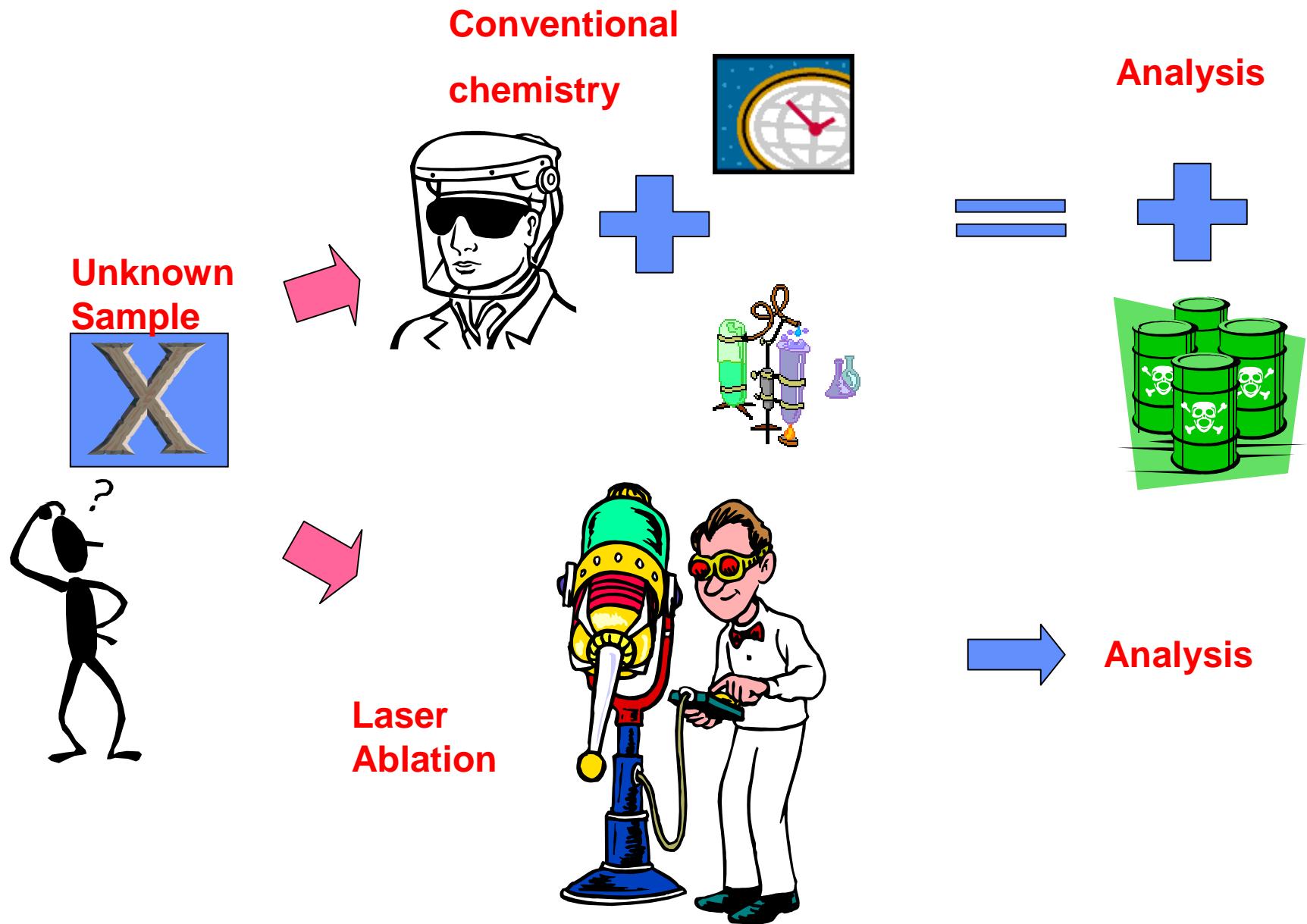
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Conclusions



- Laser ablation is an ideal technology for direct solid sample chemical analysis!
- Many results based on specific instrument
- Laser ablation produces particles! “Duh” (H. Simpson)
- ‘Better’ is relative - based on application and availability
- Femtosecond laser ideal for studying laser ablation
- Fundamental – modeling studies needed
 - Bogaerts A. Chen ZY. Gijbels R. Vertes A. Laser ablation for analytical sampling: what can we learn from modeling? *Spectrochimica Acta Part B-Atomic Spectroscopy*. 58(11):1867-1893, 2003.
- The chemistry is critical!
 - Influence of chemistry on ablation, plasma properties, particles
 - Influence of plasma on ablation

Ultimate Goal →





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